PHYSICAL CHEMISTRY
FOR SCHOOLS

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by

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PREFACE

THIS little book is intended to serve as a brief introductory outline of Physical Chemistry for the use of students who have been through the very elementary courses of descriptive Chemistry and Physics.

The subject-matter is given, as far as possible, in the form of concise, direct statements; long detailed explanations, historical introductions and mathematical formulae being avoided as far as possible. It is hoped that by introducing the subject in this way it may be possible to fix the attention and to stimulate interest in the case of many students who, as experience shows, are liable to be scared away from the subject when it is presented in the more elaborate and mathematical form.

It will be understood, of course, that in the study of Physical Chemistry many important problems and theories occur which are, perhaps, beyond the capabilities of elementary students. Matters of this kind have been only briefly sketched and are given in sections printed in smaller type, so that they can be used at the discretion of the teacher.

The author desires to express his sincere thanks to Mr W. H. Mills, M.A., Ph.D., for his kindness in reading the proof-sheets and in making many useful suggestions; and to Dr Shillington Scales for executing the diagrams.

<div style="text-align: right">H. J. H. F.</div>

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CHAPTER I

ELEMENTS, COMPOUNDS AND MIXTURES

1. All known substances may be initially classified as (*a*) chemical individuals or (*b*) mixtures. The chemical individuals are further distinguished as "elements" and "compounds," and the mixtures may be either "homogeneous" or "heterogeneous." These terms being of considerable importance it will be advisable to give here a brief introductory account of their meaning.

Chemical individuals are characterised by having a definite and fixed composition and their composition remains, in general, unchanged when they change their physical state—e.g., from solid to liquid or liquid to gas—even though the external conditions are varied.

The term *hylotropic* substance is used to denote a substance which can change its physical state without change of composition; but a hylotropic substance is not necessarily a chemical individual. The distinction lies in the fact that a chemical individual remains hylotropic, within certain limits, even though the conditions (pressure, temperature, etc.) change.

Mixtures have a variable composition; a little more or less of one or other constituent does not alter the general character of the mixture, and the constituents may, as a rule, be easily separated, often by purely mechanical processes. Their properties are generally *additive*, that is to say, they retain the properties of their constituents, each constituent conferring its own properties on the mixture in proportion to the quantity of it which is present.

An **element** has hitherto been defined as a substance which *up to the present* has not been decomposed into anything simpler. The term did not imply that the substance *could not be*, only that it *had not been*, decomposed; if someone succeeded in decomposing it, it ceased to be called an element. "Until a body is decomposed, it should be considered simple" (Davy, 1811). Numerous instances may be given of this: caustic potash was regarded as an element until Davy, in 1808, got potassium out of it, and didymium was always supposed to be an element until Auer von Welsbach, in 1885, succeeded in obtaining two distinct substances from it. But many chemists now consider that this original definition of "element" must be abandoned in view of the theory which, at present, accounts for the remarkable properties of radioactive substances. Radium, for instance, behaves in most respects exactly like an element of the second group, its general chemical characters resembling closely those of barium. Yet radium undergoes spontaneous decomposition and helium and various other products arise from it. If we adhere to the original conception of the term therefore, radium is not an element. If we wish to regard it as an element, we must alter the definition of the term. Considerable difference of opinion has existed with regard to this point, but it is, after all, merely a question of words.

Chemical compounds have a fixed and invariable composition and have *specific properties*; properties, that is to say, which are distinct from those of the constituents and are peculiar to the compound itself. The separation of a chemical compound into its constituents cannot be effected by mechanical processes (such as filtration, sorting out, etc.), nor, as a rule, by simple physical processes such as distillation, freezing, melting; this distinction however is not always sharp. A most important characteristic of a chemical compound, as distinct from a mixture, is the fact that the composition by weight is always simply related to certain constant numbers

peculiar to each constituent. In other words, to each constituent one may assign a constant number such that the composition of any chemical compound, containing these constituents, may be represented either as the sum of these constants or as the sum of simple multiples of them. Thus to oxygen we may assign the constant 8, to chlorine 35·5, and to sodium 23. For we find that in sodium monoxide and dioxide the composition is 23 of sodium to 8 and 2 × 8 of oxygen respectively; in sodium chloride the composition is 23 of sodium to 35·5 of chlorine, and in sodium hypochlorite 23 of sodium, 35·5 of chlorine and 16 of oxygen. We may express this in a general way by saying that to each of the elements, A, B, C... we may assign a constant number E_1, E_2, E_3... such that the composition of any compound may be represented as $aE_1 + bE_2$ or $aE_1 + bE_2 + cE_3$, and so on, where a, b, c... are, in general, small whole numbers. The actual numbers used to denote these constants will, of course, depend on the unit chosen. It would no doubt be simplest to take that constant as unity which is found to have relatively the smallest value, i.e., the constant assigned to hydrogen would be exactly 1; this system is often adopted and it has certain advantages. But there are reasons, both practical and theoretical, for preferring the system which assigns the exact number 8 to oxygen; on this system the constant for hydrogen will be 1·008 instead of 1.

The term *equivalent weight* of a substance is used in chemistry for that weight of the substance which can combine with or replace a given weight of some other substance taken as standard; in terms of the generalisation given above, it will be a matter of indifference whether we take as standard 8 parts of oxygen, 1·008 of hydrogen, or 35·5 of chlorine, etc. It is evident that one element may often have more than one equivalent weight. 35·5 parts of chlorine, for example, may combine with either 200 parts or 100 parts of mercury. When this happens the different values of the equivalent weight are always simply related to one another, i.e., they are

simple multiples of a common factor (law of multiple proportions).

2. Homogeneous and heterogeneous mixtures. A substance is said to be homogeneous if every part of it is (as far as can be ascertained by practical tests) identical in composition and in chemical and physical properties with every other part; otherwise it is heterogeneous. The constituents of a heterogeneous mixture, in most cases, can be separated by mechanical processes, such as sorting out, filtration or sedimentation; when such processes fail the parts can be made evident by means of the microscope or the "ultramicroscope" (see Section 29). The distinction is, in ordinary cases, quite simple, but if the subdivision of a substance is very great, i.e., if it is present in extremely minute particles, it becomes difficult or impossible to draw a sharp line between a homogeneous and a heterogeneous system*. In certain colloidal solutions, for example, particles may be present which can be distinguished by the microscope, others only by means of the ultramicroscope; in addition to these there is sometimes indirect evidence of still smaller particles which cannot be observed at all. According to the molecular theory, all matter has a "grained" structure, and if our means of observation were sufficiently powerful we should be able to distinguish distinct parts, with a surface of separation between them, in all substances. In this sense all matter would be heterogeneous. The terms are generally used however only in the strictly practical sense outlined above.

The different parts of a heterogeneous system which are themselves homogeneous are called *phases*. Thus we refer to a gas, or a mixture of gases, as a one phase system; ice and water, a two phase system; and ice, water and vapour as a three phase system. Homogeneous mixtures, the composition of which can be continuously

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* The material or collection of materials under consideration is referred to as a *system*.

varied, at any rate between certain limits, are called *solutions*. We may have solutions of solids in liquids, liquids in liquids, solids in solids, and so on.

3. Polymorphism, Allotropy and **Isomerism.** Many instances are known of substances which have the same composition but different properties; such cases are classified under various names, as follows:

Polymorphous substances are those which in the solid state are known to exist in more than one crystalline form. The different crystalline forms of a substance usually have marked differences in physical properties, such as density, melting point, etc. Well-known examples are rhombic and monoclinic sulphur, white and red phosphorus, diamond and graphite, and the different crystalline forms of calcium carbonate, iodine chloride, monochloracetic acid, etc. (Some writers include the amorphous forms of a substance amongst the polymorphous forms, e.g., viscous sulphur and charcoal*.)

Allotropy. The polymorphous varieties of an *element* are referred to as *allotropic forms* or allotropes. The term is commonly used, however, for all modifications of an element which exhibit different properties, whether they are solids or not; thus ozone is called an allotropic modification of oxygen.

Isomeric compounds are those which have the same composition and the same molecular weight (Section 11) but different properties. They are further classified under several heads, such as structural isomerides, stereo-isomerides, etc.; these terms are best considered in connection with the study of Organic Chemistry.

Polymeric substances are those which have the same composition but molecular weights which are simple multiples of one another. Examples are the different states in which elements such as iodine and sulphur are known to exist as vapour (I_2 and I, S_8 and S_2, etc.); cyanic acid $HCNO$ and cyanuric acid $H_3C_3N_3O_3$; aldehyde

* See also page 10.

C_2H_4O and paraldehyde $C_6H_{12}O_3$; acetylene C_2H_2 and benzene C_6H_6. [Note that the term is, as a rule, only used for those substances which can be directly converted one into the other, e.g., one does not call acetic acid $H_4C_2O_2$, a polymeric modification of formaldehyde, H_2CO.]

A large number of elements exhibit allotropy; the most familiar cases occur amongst the non-metals, and it was at one time thought that allotropy was peculiar to non-metals. But recently several important examples have been discovered amongst the metals, e.g., iron, tin, etc. The differences in properties between the allotropic modifications of an element are often exclusively of a physical kind such as crystalline form, density, solubility, melting point, heat of combustion; but in some cases there is a notable difference in the properties usually classed as chemical, e.g., ozone acts as a much more powerful oxidising agent than oxygen, and white phosphorus is much more easily oxidised than red phosphorus. The cause of allotropy is unknown; it is usually ascribed either to a difference in the arrangement or in the mode of aggregation of the molecules or to a different number of atoms in the molecule. In the case of ozone and oxygen, we can prove that the molecules contain a different number of atoms, but with elements in the solid state we have no certain way of doing this. (See page 10.)

4. Transformation of one form into another. When a solid substance is capable of existing in two or more forms, it generally happens that at a given temperature only one of the forms is stable; this form persists, showing no tendency to change even if kept for an indefinitely long time. The other forms are, as a rule, unstable with respect to this form, that is to say, they tend to pass spontaneously into it. But the *rate* at which this change takes place varies very greatly in different cases and also under different conditions. Often the less stable form may persist for a long time, sometimes days, months

or years, without any perceptible change taking place. The system is then said to be *metastable*, or to be in a state of "suspended transformation." In other cases the less stable modification changes rapidly and spontaneously to the stable form; it is then said to be *labile* or unstable.

The change from the metastable to the stable condition can in most cases be caused to take place quickly if a trace (or "nucleus") of the stable form is added, i.e., the nucleus converts the metastable system into an unstable system. This phenomenon is easily studied in the case of supersaturated solutions (Section 19). Ordinary white tin is the metastable form of tin at ordinary winter temperatures; it remains in this state indefinitely, unless considerably cooled; if, however, a trace of the grey modification is brought into contact with it, the whole soon changes to grey tin.

The change may also be greatly accelerated, in many cases, by the addition of certain foreign substances (catalysts). Thus ordinary white phosphorus, which is the metastable modification, remains apparently unchanged for years at the ordinary temperature, although at a temperature of about 260° it rapidly changes to red phosphorus. But at much lower temperatures the change takes place with great rapidity if a trace of iodine is added.

5. For a solid substance capable of existing in two forms there is, in many cases, a definite temperature above which one form is stable and below which the other form is stable. This temperature is called the transition temperature or *transition point*. At this point only can the two forms exist together in equilibrium. For example, rhombic sulphur is the stable form below 95·5° and monoclinic sulphur is the stable form above this temperature. The grey tin is the stable form below 18·5° and white tin is stable above this temperature. The transition point is perfectly fixed and definite at a given pressure. If the

pressure is changed the transition point changes, but comparatively slightly for great difference of pressure. Thus the transition point of sulphur which is 95·5° at a pressure of one atmosphere changes to 151° at a pressure of 1288 atmospheres. The direction of this change is easily remembered; if the form stable below the transition point has a greater density than the form stable above it, *increase* of pressure will *raise* the transition temperature, and conversely. Rhombic sulphur is more dense than monoclinic sulphur and water is more dense than ice; increase of pressure raises the transition point of sulphur and lowers the melting point of ice.

In the cases referred to, such as tin and sulphur, we see that the process of changing one form into the other is directly reversible; we can obtain either form as the stable one by suitably fixing the temperature. Substances which behave in this way are called *enantiotropic*. There is another class of substances in which only one form is stable at all temperatures below the melting point, the other form being metastable. In this case there is no transition point, or if there is, it cannot be observed, since it would lie above the melting point. Such substances are called *monotropic*. Iodine monochloride and phosphorus may be mentioned as examples. Thus, white phosphorus is always metastable with respect to red phosphorus; we cannot transform red phosphorus into white phosphorus by merely altering the temperature of the solid. We can do so however if we vaporise it and quickly cool the vapour.

When a substance capable of existing in two or more forms is produced in a chemical reaction, or is obtained by condensation of its vapour, it is always the *less* stable modification which first makes its appearance and this less stable form then quickly or slowly changes to the stable form. The production of white phosphorus, or yellow arsenic, by condensation of the vapours, are instances of this. Mercuric iodide, again, can exist in two forms, yellow and red. The yellow form is stable above 126°,

and the red form is stable below this temperature. If now either form be vaporised and the vapour condensed on a cold surface, the *yellow* form is obtained and remains for a considerable time; pressure however causes it to change at once into the red form. Similarly, on precipitating mercuric iodide, by adding potassium iodide to mercuric chloride, in solution, the yellow form first appears; but, in this case, it quickly and spontaneously changes.

As regards the general properties of the stable and unstable forms of a substance, it may be observed that the *less* stable form always has the greater solubility, the greater vapour pressure and the lower melting point. The modification more stable at the ordinary temperature usually has the greater density. The heat of combustion is also less for the more stable form, as might be expected, since energy has to be expended in converting the more stable to the less stable form.

When an element which can exist in two forms in the solid state is liquefied, there is, as a rule, no longer any evidence of more than one form; ozone and oxygen in the solid state form an exception to this. According to Smith, in liquid sulphur there appear to be two modifications (called S_λ and S_μ) which are present in a state of equilibrium, the proportions varying with the temperature. In this case there appears to be a certain temperature (160°) at which the two liquids cease to be completely miscible and the mixture separates into two phases.

In compounds, several cases are known in which the liquid may consist of two modifications present together in a state of equilibrium. Acetoacetic ester is a well-known example.

In these cases there is, of course, no transition point; both modifications may exist in a state of stable equilibrium throughout a considerable range of temperature and at each temperature there is a definite ratio between the quantities of the two forms present.

Considering the close resemblance between liquid solutions and solid solutions (Section 28) it is, of course, possible that equilibrium mixtures of two modifications of an element might exist in the solid state and it has been suggested that some cases of allotropy may be of this nature.

It is now generally the custom to restrict the term *polymorphism* to those cases in which the difference in properties between the solid modifications of a substance are supposed to be due to a different arrangement of the identical molecules in the crystals (*a*). If the difference in properties is ascribed to a different structure of the molecules themselves, i.e. to a different arrangement or number of the atoms in the molecules (*b*), the terms isomerism, tautomerism, polymerism, etc., are used.

It is sometimes difficult or even impossible to decide between the two cases (*a*) and (*b*). If the different solid modifications when dissolved or liquefied yield identical liquids, the modifications are usually regarded as polymorphous, in the above sense. In the case of isomeric, etc., substances, the differences still persist in the liquid state, at any rate for a time.

CHAPTER II

GASES

6. A gas has the characteristic property that a given mass of it will fill any vessel no matter what its size or shape. Different gases are always miscible in all proportions, even if they are of different densities, so that a uniform mixture will tend to result; a heterogeneous gas mixture, in equilibrium, is an impossibility. The laws which regulate the behaviour of gases under varying temperatures and pressures are the same for all gases; this is a peculiarity of gases since liquids and solids behave differently according to their nature, e.g., each liquid or solid has its own specific coefficient of expansion, etc.

These laws may be formulated in the following way:

(1) *Boyle's law.* The volume of a given mass of gas, at a given temperature, varies inversely as the pressure. Thus if V_1 is the volume at P_1 the volume at P_2 will be

$$V_2 = \frac{V_1 P_1}{P_2} \text{ or } V_1 P_1 = V_2 P_2.$$

(2) *Gay Lussac's law* (sometimes called Charles' law). The volume of a given mass of gas, at a given pressure, increases $\frac{1}{273}$ of its volume at $0°$ for a rise of $1°$. If therefore a gas were cooled to $-273°$ and if it continued to obey this law, its volume would be reduced to nothing. This temperature, $-273°$, is called the absolute zero and temperatures reckoned from it are called absolute temperatures; for example, $15°$ C. is $273 + 15°$ absolute.

Using this term, we may state Gay Lussac's law as follows: The volume of a given mass of gas at a given pressure varies directly as the absolute temperature. Thus if V_1 is the volume at $t_1°$, the volume at $t_2°$ will be

$$V_2 = V_1 \frac{273 + t_2}{273 + t_1}, \quad \text{or} \quad \frac{V_1}{273 + t_1} = \frac{V_2}{273 + t_2}.$$

(3) If the volume of a gas is kept constant and the temperature is altered, the pressure will vary directly as the absolute temperature. If P_1 is the pressure at $t_1°$, the pressure at $t_2°$ will be

$$P_2 = P_1 \frac{273 + t_2}{273 + t_1}, \quad \text{or} \quad \frac{P_1}{273 + t_1} = \frac{P_2}{273 + t_2}.$$

The three laws may be expressed in one relation, namely

$$\frac{V_1 P_1}{273 + t_1} = \frac{V_2 P_2}{273 + t_2},$$

or simply, as $VP = RT$, where T is the temperature on the absolute scale and R is a constant. For a given volume of gas measured at the same temperature and pressure, R has the same value for all gases and the number which it expresses will depend only on the units chosen and the quantity of gas.

6 a. It is very convenient for the purpose of chemical calculations to take as the standard volume, the space filled by 32 grams of oxygen at 0° and 760 mm. The reason for this will be explained later. This volume is 22·4 litres, i.e., 22,400 cubic centimetres. When the barometer stands at 760 mm., the atmospheric pressure is equal to the weight of 76 cubic centimetres of mercury on the square centimetre; the density of mercury being 13·6, this weight is 76 × 13·6 grams. The pressure of the atmosphere is therefore 1033·3 grams per square centimetre. In these units then

$$R = \frac{22,400 \times 1033 \cdot 3}{273} = 84,760.$$

In absolute units, the atmospheric pressure will be 1033·3 × 981 dynes per square centimetre, i.e. a little over a million dynes per square centimetre and R will be about 83 millions.

It frequently happens in chemical calculations that we have to find the work done in producing a given quantity of a gas under a constant pressure. This work is measured by the product of the volume and pressure. Similarly, if a gas expands from the volume V_1 to V_2 at a constant pressure of P, the work done is $P(V_2 - V_1)$. The product VP therefore measures a quantity of energy and we can express this in mechanical units or in heat units. The numerical value of R in the above equation, expressed as work in mechanical units, is 84,760 gram centimetres (or about 83 million ergs). If we wish to express this as heat units, we must divide by the mechanical equivalent of heat, which, for the gram centimetre, is 42,720 calories. The value of R then becomes $\dfrac{84,760}{42,720}$ or approximately 2 so that, with sufficient accuracy for most purposes, we can write the gas equation as

$$PV = 2T.$$

The equation shows us that the work done in producing a given quantity of a gas is proportional to the absolute temperature and is independent of the pressure. If we generate 32 grams of oxygen at 0° the volume will be 22,400 c.c., if the pressure is one atmosphere, and the work will be 22,400 × 1033·3 gram centimetres; whereas, if the pressure is two atmospheres, the volume will be 11,200 and the work will be the same as before, namely, 11,200 × 2066·6 gram centimetres.

The work done by a gas in expanding from V_1 to V_2 is as above stated, $P(V_2 - V_1)$, if the pressure has the constant value P. If the pressure is not constant, the calculation is more complicated. See Section 12.

7. Liquefaction of gases.

It is generally the custom to call a given substance a "gas" if it happens to be gaseous at the ordinary temperature and pressure; if under these conditions the substance is a solid or liquid, we speak of its gaseous form as a "vapour." But there is no essential difference between the two; all gases have now been liquefied and all except helium have been solidified.

A substance which exists as a gas at ordinary temperatures and pressures may be converted into a liquid if the temperature is sufficiently lowered and if the pressure is not too small. If we subject a gas to gradually increasing pressures, at a given temperature, its volume will become increasingly smaller, and on continuing to

increase the pressure, one of two things may happen: (1) it may either continue to diminish in volume and remain homogeneous, or (2) it may at a certain pressure separate into two phases, liquid and gas. Which of these two things happens will depend on the temperature. For each gas there is one definite temperature above which no amount of pressure will ever liquefy it. This is called the *critical temperature*. At any temperature below this, it can be liquefied if the pressure is sufficient; and the lower the temperature the less will be the pressure required to liquefy it. At the critical temperature the pressure required to liquefy it is the greatest that is ever required; this pressure is called the *critical pressure*. It may be defined as the pressure which will just be sufficient to liquefy the gas at the critical temperature or as the maximum pressure at which the liquid and vapour can exist together in equilibrium.

A substance which is at the critical temperature and under the critical pressure is said to be at the *critical point*. At this point the properties of the gas and liquid show no discontinuity and the density of the liquid is the same as that of its saturated vapour. The density of the substance at this point is called the *critical density* and the reciprocal of this is the *critical volume*. The critical temperature of carbon dioxide is about 31° and the critical pressure is 73 atmospheres. At 21° carbon dioxide can be liquefied by a pressure of about 60 atmospheres, at 13° by 50 atmospheres and at 0° by about 35 atmospheres. Sulphur dioxide, whose critical temperature is 155°, can easily be liquefied at ordinary atmospheric pressure if cooled to about $-9°$.

The gases first liquefied were sulphur dioxide, chlorine, ammonia, nitrous oxide, carbon dioxide and some others. All attempts to liquefy oxygen, hydrogen, nitrogen, carbon monoxide, nitric oxide and marsh gas were at first unsuccessful and these used to be called the six "permanent" gases. Before critical phenomena were recognised, it used to be thought that these gases might be

liquefied if sufficiently great pressures were used, and experiments were made at enormous pressures; but these failed because the temperatures used were above the critical temperature. For the purpose of liquefying gases, the *cooling* is the most important condition; the pressures required are never very large, seldom exceeding 100 atmospheres. At the boiling point of hydrogen, all gases, except helium and hydrogen, liquefy or solidify at atmospheric pressure. The methods used for cooling the more difficult liquefiable gases depend on (1) the rapid boiling of liquids, (2) the expansion of gases, both with and without the performance of work.

Thus Pictet (1877) succeeded in liquefying oxygen by first using liquid sulphur dioxide boiling under reduced pressure to liquefy carbon dioxide; and by boiling this liquid under reduced pressure he reached a temperature of about $-140°$. The critical temperature of oxygen is $118·8°$ and at the temperature reached the gas liquefied under the pressure produced by generating the gas in a closed vessel.

Cailletet, about the same time, obtained air, oxygen, nitrogen, carbon monoxide and marsh gas in the liquid state by strongly compressing the gases and suddenly releasing the pressure. Under these circumstances, the gas does work against the atmospheric pressure and the energy required for this is taken from the gas itself and its temperature consequently falls. Hydrogen treated in this way gave a "mist," indicating incipient liquefaction.

The method of cooling the gases which is now generally adopted depends on a totally different principle, namely, that when a strongly compressed gas is allowed to escape through a small hole, or porous plug, without doing external work, it becomes cooled. This cooling, known as the *Joule-Thomson effect*, depends upon the fact that the compressed gas disobeys Boyle's law in the direction referred to in Section 8. The cooling is due to the work performed in overcoming the mutual attraction of the molecules, and the energy required for this is taken from

the gas itself.   This effect is more pronounced the lower
the initial temperature of the gas, so that in applying
this method it is an advantage to cool the gas to start
with. [Hydrogen, as stated below, at ordinary tem-
peratures, deviates from Boyle's law in the opposite
direction to most other gases, but the direction of this
deviation changes at about $-80°$. It is only below this
temperature that the effect mentioned can be obtained.]

In making use of this effect for the purpose of lique-
fying gases, the dried gas is compressed to about 200
atmospheres and is sometimes initially cooled by means of
a freezing mixture.   It is then allowed to expand through
a valve and in doing this, its temperature is further lowered
in accordance with the above principle.   The cold gas
thus obtained is now caused to travel backwards so as to
cool the remaining compressed gas; this escaping through
the valve becomes still further cooled, and so on.

8. Deviations from the gas laws. No gas obeys Boyle's law
exactly, although at ordinary temperatures and low pressures the
agreement is very close.   As the pressure increases, the deviations
become more pronounced, the product PV instead of remaining
constant, changes.   At ordinary temperatures, in the case of all
gases except hydrogen, helium and neon, the value of PV at first
decreases as the pressure increases, that is to say, the gas is more
compressible than it would be if it obeyed Boyle's law.   But if
the pressure is continually increased, a limit is reached beyond
which the value of PV increases as the pressure increases. Hydrogen,
helium and neon at ordinary temperatures are always less com-
pressible than they would be if they obeyed Boyle's law, i.e. PV
always continuously increases as the pressure increases; at very
low temperatures however, their behaviour resembles that of other
gases, showing a minimum when a certain pressure is reached.

These deviations can be explained very clearly in terms of a
theory introduced by van der Waals in 1881.   The behaviour of
most gases at high pressures, and of hydrogen, helium and neon,
in which the product PV increases with increasing pressure, can be
accounted for if the gas is considered to behave as if it consisted of
an incompressible part (b) and another part $(V - b)$ and that only
this compressible part obeys Boyle's law.   As a result of this, the
greater the pressure is, the smaller will be the proportion of the total
volume which is occupied by the compressible part.   The molecules,
that is to say, will have less space to move about in than is assumed

by Boyle's law and, consequently, for a given diminution of the total volume, the pressure will be greater than this law requires; the product PV will therefore increase as the pressure increases. The "incompressible volume," (b), depends on the space actually occupied by the molecules themselves. (On theoretical grounds it has been considered that (b) is four times the space occupied by the molecules.)

In addition to this correction, it is necessary to consider that the molecules have an attraction for one another, and this attraction will evidently be more considerable as the concentration of the gas becomes greater. Van der Waals assumes that the attraction is proportional to the square of the density of the gas, or, in other words, is inversely proportional to the square of the volume. The effect of this attraction is that the volume of the gas at the observed pressure P is less than it should be according to Boyle's law; the volume will be the same as if we added an *increase* to the pressure P and the gas obeyed Boyle's law. This increase can be represented as the factor $\frac{a}{V^2}$ where a is a constant depending on the nature of the gas and on the temperature. Introducing these two corrections, the gas equation $PV = RT$ becomes $\left(P + \frac{a}{V^2}\right)(V - b) = RT$.

The two corrections $\frac{a}{V^2}$ and b act therefore in opposite directions, the observed value of PV being diminished by the attraction effect and increased by the volume effect. In explanation of the deviations referred to above, it may be supposed that for most gases at relatively low pressures, the attraction correction is more pronounced than the volume correction, but when the pressure reaches a certain sufficiently high value, the volume correction (b) overbalances the attraction correction. In the case of hydrogen, helium and neon, at ordinary temperatures, the volume correction is, at all pressures, more pronounced.

If van der Waals' equation is multiplied out and arranged in powers of V, it becomes

$$V^3 - V^2\left(b + \frac{RT}{P}\right) + \frac{aV}{P} - \frac{ab}{P} = 0.$$

This being an equation of the third degree, it has either one or three real roots; for every value of T and P there are either one or three values of V. In case of the gas alone at low pressures or the liquid alone at high pressures, there is only one value, but for temperatures at which the substance exists both as gas and liquid there are evidently two values. The third volume cannot be observed experimentally as it would represent an unstable condition of the substance.

At the critical point, the densities, and therefore the specific volumes of the liquid and vapour, become equal and the unrealised "third volume" is also equal to these. The three values of V are therefore identical at the critical point and V at this point is defined as the critical volume. By algebraical transformations we can find the values of the critical volume, V_0, the critical pressure, P_0, and the critical temperature, T_0, in terms of the constants a, b and R. These become

$$V_0 = 3b, \quad P_0 = \frac{a}{27b^2} \quad \text{and} \quad T_0 = \frac{8a}{27Rb}.$$

If now instead of expressing the values of the volume V, pressure P and temperature T in the usual units, we express them as fractions of the critical values, that is

$$\phi = \frac{V}{V_0}, \quad \pi = \frac{P}{P_0} \quad \text{and} \quad \theta = \frac{T}{T_0},$$

and introduce these values into the van der Waals' equation, and substitute the above values for the critical constants, we obtain

$$\left(\pi + \frac{3}{\phi^2} \right) (3\phi - 1) = 8\theta.$$

Here a, b and R have been eliminated and the equation expresses a general relation, both for gases and liquids, which is independent of the nature of the particular substance (provided no association or dissociation occurs).

The values $\frac{V}{V_0}$, $\frac{P}{P_0}$ and $\frac{T}{T_0}$ are usually called the *reduced* volume, pressure and temperature respectively. If in any two substances the reduced temperatures are equal, the substances are said to be at *corresponding* temperatures. Thus if $\frac{T}{T_0} = \frac{T'}{T_0'}$, T and T' are corresponding temperatures (absolute). Similarly, with the pressures and volumes. Again, if in two substances the reduced volumes, pressures and temperatures are equal, respectively, the two substances are said to be in *corresponding states*.

In comparing the properties of substances it would appear that the most suitable conditions for comparison are those which "correspond" in this sense, since the reduced values when introduced into van der Waals' equation give a relation which is independent of the properties of particular substances.

Suppose, for example, that we have determined some physical property of a substance at a particular temperature, t, and we wish to compare this property in a second substance at a "corresponding" temperature.

If T_0 is the critical temperature (on the absolute scale) of the first substance and T_0' is that of the second substance, the temperature x at which the comparison should be made is found by the relation

$$\frac{273 + t}{T_0} = \frac{273 + x}{T_0'}.$$

9. Laws of combination of gaseous substances by volume. Gay Lussac and Humboldt in 1805 first found that the volumes of hydrogen and oxygen which combine to form water are in the ratio of $2 : 1$ and Gay Lussac, later, showed that in many other combinations of gaseous substances simple relationships hold. His law may be stated in two parts, as follows: (a) when gaseous substances combine together or react with one another, chemically, the volumes so combining or reacting stand to one another in a simple ratio; and (b) if the resulting product is also gaseous, its volume stands in a simple relation to the volumes of the gases which produced it. The gases are, of course, measured at the same temperature and pressure.

It has been stated above (page 2) that the weights of substances which combine or react chemically stand to one another in some simple relation to their equivalent weights; consequently it follows that equal volumes of different gases must contain either the same number of equivalent weights or multiples of these by small whole numbers. Dalton in 1803 quantitatively developed the theory, which had been suggested in a somewhat indefinite way by the ancient Greek philosophers, that matter is made up of small indivisible parts or *atoms*. If this is so it is evident that the relative weights of the atoms must be simply related to the equivalent weights. Now it was at first supposed that Gay Lussac's law of volumes could be explained if we consider that equal volumes of gases contain the same number of atoms, the word atom being then used in reference to compounds as well as to elements. But the composition by volume

2—2

of hydrochloric acid and of water showed that this sup-
position is not admissible; thus one volume of hydrogen
and one volume of chlorine give rise to two volumes of
hydrogen chloride, so that, if equal volumes of each of
these gases contained the same number of atoms, one
atom of hydrogen would give rise to twice as many atoms
of hydrogen chloride; which, of course, is absurd, since
each atom of hydrogen chloride must contain at least
one atom of hydrogen.

Similarly with water, one volume of oxygen when
combined with hydrogen yields two volumes of water
vapour; hence on the above supposition, a given number
of oxygen atoms would yield twice as many atoms of
water, whereas, by definition of an atom, one atom of
water cannot contain less than one atom of oxygen.

Molecules. A way out of these difficulties was suggested
by Avogadro in 1811 and by Ampère in 1812, by making a
distinction between the ultimate indivisible parts or atoms,
and the parts which move about as wholes in the gas.
The latter *may* consist of single atoms, but in most cases
they consist of two or more atoms combined together.
These independently moving particles are called mole-
cules. The hypothesis of Avogadro, or "Avogadro's
law" as it is usually called, may then be stated in the
usual way as follows: equal volumes of all gases at the
same temperature and pressure contain the same number
of molecules. In the above examples we now say, in
accordance with Avogadro's hypothesis, that one mole-
cule of hydrogen gives rise to two molecules of hydrogen
chloride and one molecule of oxygen yields two molecules
of water vapour.

10. Kinetic theory of gases. The regular behaviour of gases
under the influence of temperature and pressure, the diffusion of
gases and most of their other general properties, can be explained
in a purely mechanical way if we consider that a gas consists of
small individual parts, or molecules, in a state of rapid motion.
For the same gas the mass of each molecule is supposed to be the
same. The molecules are assumed to behave as perfectly elastic
spheres, so that on impact with the side of the containing vessel

they rebound with the same velocity as before. The molecules will be constantly colliding with one another and in doing so their velocities will alter in magnitude and direction so that the velocities will have various values. Since the space in which the molecules move is large in comparison with their size and number, each molecule will have a certain "free path" before it comes in contact with another molecule.

The pressure of a gas, according to this theory, is due to the bombardment of the molecules against the sides of the vessel and it will depend therefore on the mass M of the molecules, their number N and the velocity U with which they move. It can easily be shown that if V is the volume of the vessel and P the pressure on unit area

$$P = \frac{MNU^2}{3V} \quad \text{or} \quad PV = \frac{MNU^2}{3}.$$

The velocity U however represents a "mean" value, or, more strictly, U^2 is the mean of the squares of all the velocities. Or, we may say that U is a velocity such that the gas would have its actual kinetic energy if each of the molecules were moving with the velocity U. Mathematical calculation shows that velocities near the mean are the most common and that comparatively few molecules will be moving with very great or very small velocities. We can calculate the velocity U if we find the product MN, i.e. the density of the gas, although we do not know the values of M or N independently; it is found that, at 0°, the value for hydrogen is 1837 metres per second and for oxygen 461 metres, i.e. about a quarter of a mile per second.

If we have equal volumes of two gases at the same temperature and pressure, it follows from the above relation that

$$M_1 N_1 U_1{}^2 = M_2 N_2 U_2{}^2,$$

the mass, number and mean square velocity of the one gas being M_1, N_1 and U_1 and of the other M_2, N_2 and U_2. If now we place the two gases in communication we shall find that there is no change of temperature and pressure; from this, and for other reasons, we conclude that the mean kinetic energy of the two sets of molecules is the same. If this were not so the two gases would not be in equilibrium, one would gain and the other would lose energy and there would be a change of temperature or pressure. We may therefore write

$$\frac{M_1 U_1{}^2}{2} = \frac{M_2 U_2{}^2}{2},$$

and thus values of MU^2 in the previous equation cancel, so that we have

$$N_1 = N_2,$$

i.e., the number of molecules in equal volumes of the two gases is the same. Avogadro's law is thus deduced from the kinetic theory of gases.

11. Density and molecular weight of gases. The density of a substance is the mass of unit volume of it; the number therefore which denotes the density will depend on the units chosen. We may, for example, state the density in grains per pint or grams per litre, etc. The *specific gravity* of a substance is the density of it compared with the density of some standard substance; the number expressing the specific gravity is therefore independent of the units chosen. In chemistry the specific gravities of gases are generally referred to air, hydrogen or oxygen at the same temperature and pressure, as standard. Unfortunately, chemists are in the habit of using these terms in a loose way and the word density is employed for specific gravity referred to hydrogen as unity or to oxygen as 16. We may however use the term density in its strict sense and by choosing the gram as the unit of mass and 11·1 litres measured at 0° and 760 mm. pressure as unit volume, we obtain numbers for the density which are identical with the specific gravity referred to hydrogen as standard. Or, as is now more usual, we may take as unit volume, 11·2 litres at 0° and 760 mm.; in this case the numbers obtained are identical with specific gravities referred to oxygen as 16. Note that in many cases we speak of the vapour density of substances which are solids or liquids at 0° and 760 mm., but we can nevertheless *calculate* their densities in the way indicated above.

Since according to Avogadro's hypothesis equal volumes of all gases at the same temperature and pressure contain the same number of molecules, it is evident that the relative weights of the molecules must be proportional to the densities; or,

$$\frac{\text{molecular weight of gas } A}{\text{molecular weight of gas } B} = \frac{\text{density of } A}{\text{density of } B}.$$

We cannot by any simple method find directly the mass of a single molecule, and when we speak of molecular weight (or molecular mass) of an element or compound we mean the relative mass of its molecules compared with the mass of the atoms or molecules of some standard substance. The simplest way would be to compare the mass of the molecules with the mass of the molecules of hydrogen and then, if we can find out how many atoms there are in a molecule of hydrogen, we can express molecular weights of substances in relation to the weight of an atom of hydrogen taken as unity. It is more usual however at the present time to take the molecular weight of oxygen as exactly 32; the reason for this will be explained below. We can then write

$$\frac{\text{molecular weight of gas } A}{32} = \frac{\text{density of gas } A}{\text{density of oxygen}}.$$

But in the units above suggested, the density of oxygen is 16 and therefore

$$\frac{\text{molecular weight of gas } A}{\text{density of gas } A} = \frac{32}{16} = 2,$$

i.e., the molecular weight is twice the density.

The reasons for taking the molecular weight of oxygen as 32 are as follows:

One volume of oxygen when combined with hydrogen yields two volumes of water vapour; hence by Avogadro's hypothesis, one molecule of oxygen yields two molecules of water vapour. But each molecule of water vapour must contain at least one atom of oxygen (by definition of *atom*). Therefore one molecule of oxygen must contain *at least* two atoms. There is evidence however that the molecule of water vapour contains *not more than one* atom. Thus the oxygen in water cannot be replaced in stages; also, no gaseous compound of oxygen has ever been discovered which contains less oxygen than that which is contained in an equal volume of water vapour.

Now it is extremely unlikely (apart from direct chemical evidence) that amongst the large number of oxygen compounds known there are none which contain only one atom of oxygen in the molecule. If the molecule of water vapour contained more than one atom of oxygen, some other compound of oxygen should be found which contains less oxygen in a given volume than water vapour does, and no such compound is known.

We conclude therefore that the molecule of oxygen contains two atoms of oxygen and, since there are many reasons for fixing the atomic weight of oxygen as exactly 16 (see Chapter IV), we say that the molecular weight of oxygen is 32.

The expression *molecular weight of a substance in grams* is very often used in chemistry and this is now termed the *molar weight* of a substance or *one mol* of a substance. It is evident, employing the units indicated above, that *the molar weight of a substance is that weight of it which in the state of gas at 0° and 760 mm. would fill 22·4 litres.* If, as mentioned above, it does not happen to be a gas at this temperature and pressure, this makes no difference to the calculation; we calculate what its weight would be if it continued to exist as a gas and obeyed the gas laws.

12. It was mentioned in Section 4 that the work done in producing a volume V of a gas at a constant pressure P is measured by the product PV. Similarly, if we bring a gas from the volume V_1 to V_2 under a constant pressure P the work is $P(V_2 - V_1)$. If we produce *one mol* of any substance in the gaseous state, the volume is always the same at the same temperature and pressure, namely 22,400 c.c. at 0° and 760 mm. Introducing this value for V in the gas equation $PV = RT$ and expressing the work in heat units, we obtain $PV = 2T$ calories. That is to say, the work done in producing one mol of any substance in the gaseous state at the absolute temperature T is $2T$ calories. For example, if in some chemical reaction 32 grams of oxygen is generated as a gas at 0°, the work done in overcoming the atmospheric pressure will be equivalent to 2×273 calories.

If we bring a gas from a volume V_1 to the volume V_2 and the pressure does not remain constant, the calculation is more complicated. It can be shown by higher mathematics that if we bring

one mol of a gas from the volume V_1 to the larger volume V_2, the pressure meanwhile changing in accordance with Boyle's law, the work done is

$$RT \log_\epsilon \frac{V_2}{V_1} \quad \text{or} \quad RT \log_\epsilon \frac{P_1}{P_2}.$$

This is mentioned here because the case is of frequent occurrence in chemical calculations.

Thus in order to determine the molecular weight of a gaseous substance or of the vapour of a solid or liquid which obeys the gas laws, we have merely to find the mass m grams of it which fills a volume V c.c. at the temperature t and the pressure P. The corrected volume is then

$$V \times \frac{273}{273 + t} \times \frac{P}{760} = V_0,$$

the density is

$$\frac{m}{V_0} \times 11{,}200 = d,$$

and the molecular weight is $d \times 2$.

This method of finding the molecular weights of gaseous substances and vapours is largely used in fixing what is called the *molecular formula* of a substance. Chemical analysis alone can only tell us the "empirical" formula, that is, the formula indicating the *composition* of the substance. Thus, analysis shows that the hydrocarbons ethylene, propylene, butylene and amylene, all have the same composition which may be represented by the empirical formula $(CH_2)_x$. In order to fix the molecular formulae, we take their gaseous densities and multiply the results by 2 to obtain the molecular weights; these are found to be 28, 42, 56 and 70 respectively, showing that the molecular formulae must be written C_2H_4, C_3H_6, C_4H_8 and C_5H_{10}.

It is remarkable that amongst inorganic compounds it nearly always happens that the molecular formula found in this way is the *simplest* formula. That is to say, if we take the simplest formula weight in grams and convert it into vapour it will fill a space which, when

corrected to normal temperature and pressure, is 22·4 litres. Several cases are known in which at a certain, relatively low, temperature the molecular formula found is *twice* the simplest formula. Thus the vapour densities of ferric chloride, stannous chloride and arsenious oxide indicate the formulae Fe_2Cl_6, Sn_2Cl_4 and As_4O_6. Hydrofluoric acid also has a density too great for the simple formulae HF. But in all these cases it has been shown that at higher temperatures the densities diminish and at a sufficiently high temperature correspond to the simplest formulae.

The important question arises, by what molecular formula should such substances be represented? Obviously the answer is that if a molecular formula is used the *conditions* should be stated. This however is seldom done, and chemists are in the habit of using that particular multiple of the simplest formula which suits their views. Iodine is a good example; the formula is almost invariably written I_2, yet at very *high* temperatures its molecular formula is I; whereas hydrofluoric acid is generally written HF although at *low* temperatures its molecular formula is $(HF)_x$ where x is greater than unity.

Still more inconsistent is the common habit of representing a substance by a definite molecular formula when we know nothing whatever about its molecular weight. Examples of this are the formulae always employed for ferric oxide or silica, which should properly be written $(Fe_2O_3)_x$ and $(SiO_2)_x$.

13. So-called abnormal vapour densities. In the examples mentioned in the foregoing section the fact that the density is *greater* than that required by the simplest formula is easily accounted for; we have merely to suppose that the simplest molecules *associate* themselves together into more complex molecules. But there are many cases in which the molecular formula calculated from the vapour density is *less* than the simplest possible formula, which, of course, is absurd. Thus the vapour

densities of ammonium chloride, phosphorus penta-
chloride, sulphuric acid and chloral hydrate may reach
approximately the values $\dfrac{53\cdot5}{4}$, $\dfrac{208\cdot5}{4}$, $\dfrac{98}{4}$ and $\dfrac{165\cdot5}{4}$
which, by Avogadro's rule, correspond to the molecular
weights 26·75, 104·25, 49 and 82·75 respectively. But
since the molecular weight is necessarily the sum of the
atomic weights, these values would correspond to the
impossible formulae

$$N_{\frac{1}{2}}H_2Cl_{\frac{1}{2}}, \quad P_{\frac{1}{2}}Cl_{2\frac{1}{2}}, \quad HS_{\frac{1}{2}}O_2 \quad \text{and} \quad CCl_{1\frac{1}{2}}H_{1\frac{1}{2}}O.$$
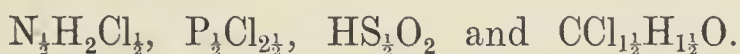
When these, and similar, cases were first observed
there was a great difference of opinion as to the
explanation of the "abnormality." Many chemists sup-
posed that with these substances Avogadro's law was
not obeyed and that there might be substances having
"two volume" formulae (i.e., those whose molecular
weight in grams fills 22·4 litres at 0° and 760 mm.) and
others having "four volume" formulae.

A much simpler way out of the difficulty is to suppose
that the vapour whose density has been determined is
not the vapour of the substance in question, but is really
a mixture of products into which the substance has been
split up by heating.

Thus ammonium chloride may split up into ammonia
and hydrochloric acid; phosphorus pentachloride into
phosphorus trichloride and chlorine; sulphuric acid into
sulphur trioxide and water and chloral hydrate into
chloral and water. In each case then we should obtain
two molecules from one molecule of the original compound,
so that, according to Avogadro's hypothesis, the volume
of the gaseous product would be twice that which would
have resulted had the original compound vaporised
unchanged and the density would consequently be half
the calculated value.

There is a certain amount of experimental evidence
which confirms this view. Thus in each of the cases
mentioned, if our hypothesis is correct, we should obtain

a mixture of two gases, or vapours, having different densities, and therefore, if they are contained in a porous vessel, one should diffuse faster than the other. This has been found to be the case; if, for example, ammonium chloride is gasified in a vessel fitted with a porous diaphragm, the gas which first diffuses through is found to be *alkaline* and the residual gas *acid*. A more convincing proof however consists in the fact that the density of the gaseous products increases if, while keeping the volume constant, we add an excess of *one* or *other* of the products into which it is assumed that the original compound dissociates. Wurtz found, for example, that at constant volume, the density of phosphorus pentachloride is greater if excess of phosphorus trichloride is previously added and it reaches nearly the normal value if a sufficient proportion of the dissociation product is added. The presence of chlorine in the vapour is also indicated by the colour.

The explanation suggested above is also borne out by the fact that the densities become more "abnormal" as the temperature is higher. Thus the density of the vapour from phosphorus pentachloride is 70 at 200°, 57·6 at 250° and 52·7 at 300°.

With regard to the case of ammonium chloride, it may be mentioned that if the substance is perfectly dry, the density of the vapour has nearly the *normal* value (Baker). Probably here the vapour is in reality already undergoing dissociation, but the process takes place slowly; if moisture is present the change proceeds quickly owing to catalytic action (see Section 69).

14. Diffusion of gases. If a gas has different densities in two parts of the same vessel, it will quickly re-arrange itself in such a way that the density becomes uniform in every part of the vessel; if a gas be suddenly put into communication with a vacuous space, the same thing will happen. Again, if a gas be placed in communication with another gas, each gas will behave in the manner

stated; that is to say that each gas will move in such a way as to equalise its own partial pressure* in all parts of the vessel. This process, called *diffusion*, takes place even if, at the beginning of the experiment, the heavier gas is at the bottom of the vessel and the lighter gas at the top. This phenomenon can only be explained by supposing that the gases consist of particles in a state of active motion, and it is evident, on this supposition, that the rate at which the process takes place, other things being equal, will depend on the velocity with which the particles move.

The quantitative study of the phenomenon of free diffusion in a vessel is difficult, but if we cause the gas to pass through a small hole into a vacuous space, or into another gas, the rate may be easily measured. Experiments show that if various gases at the same temperature and pressure are allowed to flow through a hole in a thin plate the rates at which they pass are inversely as the square roots of their densities. This phenomenon is called *effusion*. If the densities of two gases are D_1 and D_2 and their rates of effusion (i.e., the volumes which pass in a given time) are R_1 and R_2 respectively,

$$R_1 \sqrt{D_1} = R_2 \sqrt{D_2}.$$

The same law is followed if the gases pass through porous substances such as plaster of Paris or unglazed earthenware. In this case it is possible to effect a *partial* separation of a mixture of two gases having different densities. Hydrogen, for example, diffuses through such substances four times as fast as oxygen, so that, if we submitted a mixture of equal volumes of oxygen and hydrogen to this process, the gas which passed through first would be richer in hydrogen than before, since, at

* In a mixture of gases at a given pressure each constituent gas exerts and supports a part of the pressure in proportion to the amount of it which is present. Thus, if we have a mixture of four volumes of nitrogen and one volume of oxygen at a pressure of 760 mm. the partial pressure of the nitrogen is $\frac{4}{5}$ of 760 mm. and that of the oxygen is $\frac{1}{5}$ of 760 mm.

the first instant, a mixture of one volume of oxygen to four volumes of hydrogen would come through. The gas mixture left behind however would now be altered in composition, so that the relative quantities coming through would be continually altering, since the rates vary directly as the partial pressures.

By means of the above law (generally called Graham's law) it is possible to compare the densities of two gases, and if we already know the density of one the other can be determined.

14 a. The law is easily accounted for on the kinetic theory, since the rates of diffusion (R) must be *proportional to* the "mean" velocity of the molecules (U) (see page 21). In two gases at the same temperature,

$$\frac{M_1 U_1{}^2}{2} = \frac{M_2 U_2{}^2}{2},$$

and since the densities are proportional to the molecular weights, we may write $D_1 R_1{}^2 = D_2 R_2{}^2$, which is Graham's law. The actual rates of effusion are, of course, very different from the calculated values of U (see above) owing to molecular collision.

If in the effusion experiment, mentioned above, the thickness of the plate is great in comparison with the diameter of the hole, it is found that the law no longer holds; if the plate were made thick enough, the experiment would be equivalent to that of passing the gas through a long fine tube. In the latter way Graham studied the phenomenon which he termed *transpiration*. Here the relative rates at which the gases pass do not show any definite connection with their densities, the principal factor being the viscosity of the gas.

Gases may also pass through compact solids; thus hydrogen readily passes through palladium, carbon monoxide through hot iron and carbon dioxide through india-rubber. In these cases it is generally considered that the gas first forms a solution, or possibly a loose chemical compound with the solid and that it is then given off on the other side, where its pressure is less.

CHAPTER III

SOLUTIONS

15. Solutions have already been defined as homogeneous mixtures of two or more substances whose composition can be continuously varied within certain limits. The properties of the solution will, as a rule, also continuously vary as the composition alters. Thus, for example, whilst a pure liquid has a definite density, a definite vapour pressure at a given temperature and a definite boiling point and freezing point, in a solution of a substance in a liquid these properties vary very considerably according to the strength of the solution. Again, when a pure liquid vaporises or freezes, the liquid, vapour and solid all have the same composition; whereas, in general, the effect of vaporising or freezing a solution is to separate it into different constituents. Thus, on boiling a salt solution, pure water escapes, and, on freezing, pure water generally separates out; in some cases however the vapour or solid may contain both constituents, but the composition will then, as a rule, be different from that of the original solution. [There are some cases in which the vapour or solid *has* the same composition as the solution, but this can only occur under definite conditions. See below.] When a substance mixes homogeneously with another to form a solution, the process is usually regarded as a purely *physical* one, but it must be remembered that there is no absolutely hard and fast line to be drawn between chemical and physical processes

and some chemists still hold the opinion that solution consists of a kind of loose chemical combination. It is practically impossible to decide this point. In any case we have no right, without further evidence, to say that a substance continues to exist *as such* when dissolved. When ordinary sodium sulphate, $Na_2SO_4 . 10H_2O$, for example, dissolves in water, does it remain in this form, i.e., do the molecules, which move about as wholes, possess this composition? Evidence rather goes to show that, in a dilute solution at any rate, the greater part of it is broken up into constituents; possibly, however, some of these constituents may themselves be chemically combined with the water. In the case of most organic compounds, such as sugar, urea, etc., there is no indication that they break up and nothing to show whether they combine with the water or not. That a strong solution of a substance does contain *some* at any rate of that substance, as such, is rendered probable if the substance has a definite solubility. See below.

In former times the word solution was used solely in reference to substances dissolved in liquids; now, as the definition shows, we speak of solutions in liquids, solids or even gases.

It is the common custom to speak of one of the constituents of a solution as the *solvent* and the other as the *substance dissolved* or the *solute*. Although this is usually convenient, it must be remembered that it is quite an arbitrary distinction. When one constituent is in large excess of the other, the substance in excess is conveniently termed the solvent; but when the proportions are not very different, there is no particular reason for making any such distinction. Thus if we dissolve a little alcohol in a great deal of water we call the result a solution of alcohol in water; a little water in a large quantity of alcohol we call a solution of water in alcohol; but if there are about equal quantities of each, it is obviously a matter of indifference which we regard as solvent and which as solute.

16. Concentration of solutions. The *mass* of a substance (regarded as the solute) which is contained in unit *volume* of a solution is called the concentration of the solution, or the concentration of the solute in the solvent. We may, of course, adopt any convenient units of mass and volume; generally in problems of physical chemistry it is convenient to take the *molar weight* (molecular weight in grams) as unit mass and the *litre* as unit volume; i.e., we express the concentration of a solution in molar weights per litre. [Such a solution is sometimes referred to as a *normal* solution; but the student must carefully distinguish between this definition of the term and that used in volumetric analysis; a normal solution in chemical analysis means a solution containing one *equivalent* weight of the active substance in grams per litre.]

The term "strength" of a solution is used in various ways: we sometimes express the strength as mass of solute in a given *mass* or in given *volume* of *solvent*; sometimes, as mass of solute in a given mass or volume of *solution*. In the case of the less soluble gases it is usual to express the strength in *volume* of gas per given *volume* of solvent.

Note that in speaking of the *density* of a solution we mean the mass of a given volume of the *solution as a whole*. The density of a solution is a function of the concentration, but is not directly proportional to it; the way in which the density varies with the concentration will depend on the nature of the substances. Thus, for alcohol in water we find, at 0°,

Percentage of alcohol	20	40	60	80	100
Density of solution	·9756	·9493	·9072	·8603	·8062

and for caustic potash in water,

Percentage of KOH	10	20	30	40	50
Approximate density	1·08	1·18	1·29	1·42	1·54

We see from these examples that as the solution

becomes stronger the density may either increase or diminish according to the nature of the substance.

The various typical classes of solutions will now be considered.

17.　Solutions of solids in liquids. When excess of a powdered solid is placed in contact with a limited amount of a liquid solvent, and the mixture is kept constantly stirred or agitated, some of the solid will go into solution. Now it is found that, at a given temperature, the concentration of the solution continually increases up to a certain point; beyond this it will not go, so long as the solid substance is present. The solution is then said to be *saturated* and the concentration or strength of the solution so obtained is called the *solubility* of the solid in the solvent at that temperature. Note particularly that the term solubility refers necessarily to the strength of the solution when it is in equilibrium with the particular solid. If the solid is absent, there is no longer any meaning in speaking of the solubility. In order to determine the solubility of a solid in a liquid, it is first necessary to be sure that the solution is saturated and this can only be done by repeatedly determining the strength of the solution from time to time until it is found to become constant. This process often takes a long time, even weeks or months in some cases. Instead of keeping the mixture at the required temperature, one may hasten the process by bringing the mixture to some temperature at which it is more soluble (see below) and then keeping it at the required temperature—but this method is not so reliable.

Having obtained our saturated solution, the next step is to determine its strength. This may be done in many cases by evaporating a weighed quantity of the solution to dryness and weighing the residue; but it is often more convenient to determine the quantity of solute in a given weight of the solution by chemical analysis or, in certain cases, by electric conductivity. See Section 98 *a*. The

solubility may then be expressed in any of the ways suggested above, e.g., molar weights per litre of solution, grams per litre of solution, grams per gram of solvent, and so on. It is the usual custom however to express the solubilities of solids in liquids as *grams of solid which are dissolved by* 100 *grams of the solvent*.

Thus, if w grams of the saturated solution are found to contain w_1 grams of the dissolved substance, or solute, the solubility is

$$\frac{w_1 \times 100}{w - w_1}.$$

The solubilities of solids in liquids vary enormously according to the nature of the substances; thus barium sulphate is so slightly soluble in water that the presence of it in aqueous solution cannot be detected by the ordinary tests, whereas in substances like calcium chloride and caustic potash the solubility is almost unlimited. Probably there is no such thing as an insoluble substance; one must suppose, even in those cases in which all tests fail to indicate solubility, that every solid does dissolve in every liquid although the quantity may be exceedingly small. The term "insoluble substance" is generally used in the sense that the substance is so sparingly soluble that ordinary qualitative reactions fail to detect its solubility; yet in these cases more refined methods will often show that some of the substance dissolves. Thus, by the conductivity method it can be shown that at ordinary temperatures about 2·3 milligrams of barium sulphate dissolves in a litre of water.

Very few definite relationships between the solubility of substances and their chemical nature have been observed. We often find, however, that elements are more soluble in liquid compounds which contain them as constituents, e.g., phosphorus in phosphorus trichloride, sulphur in carbon disulphide. Also, that organic compounds containing the hydroxyl group generally dissolve in water and that their solubility is greater as they contain a greater

3—2

number of hydroxyl groups in the molecule [e.g., compare the solubilities of benzene, phenol, hydroquinone and pyrogallol in water]. Sometimes also there are definite relations between solubility of salts and the atomic weights of the elements in them.

18. Influence of temperature on solubility. In the majority of cases solids become more soluble in liquids as the temperature is higher; this however is by no means always the case, many solids being less soluble at higher temperatures. In some cases also, a maximum or minimum is reached beyond which the direction appears to be reversed.

In order to illustrate the behaviour in this respect of some common substances, the following diagram may be given. In this the temperatures are plotted as *abscissae* (horizontal lengths from AB) and the solubilities as *ordinates* (vertical heights from AC).

We see from this that the influence of temperature may make a very great difference as in the case of lead nitrate, or a very slight difference, as with sodium chloride.

The curve for sodium sulphate shows a sharp change of direction at 32·5°. It used to be supposed that this was due to a sudden change taking place in the solution; in reality, it is due to the fact that solid hydrated sodium sulphate loses its water of crystallisation at this temperature. The two lines therefore represent the solubilities of two entirely different solids. Remember that the term "solubility" of a solid refers to the equilibrium between that particular kind of solid and its saturated solution. Whenever a sudden break occurs in a solubility curve, it shows that the *solid* has undergone change at this temperature.

There is nothing in the nature or composition of a substance which will enable us to predict whether its solubility will increase or diminish with rising temperature. There is an important relation however between

the influence of temperature on the solubility and the *heat of solution* of a substance. This relation, which is an excellent example of a very important general law (see
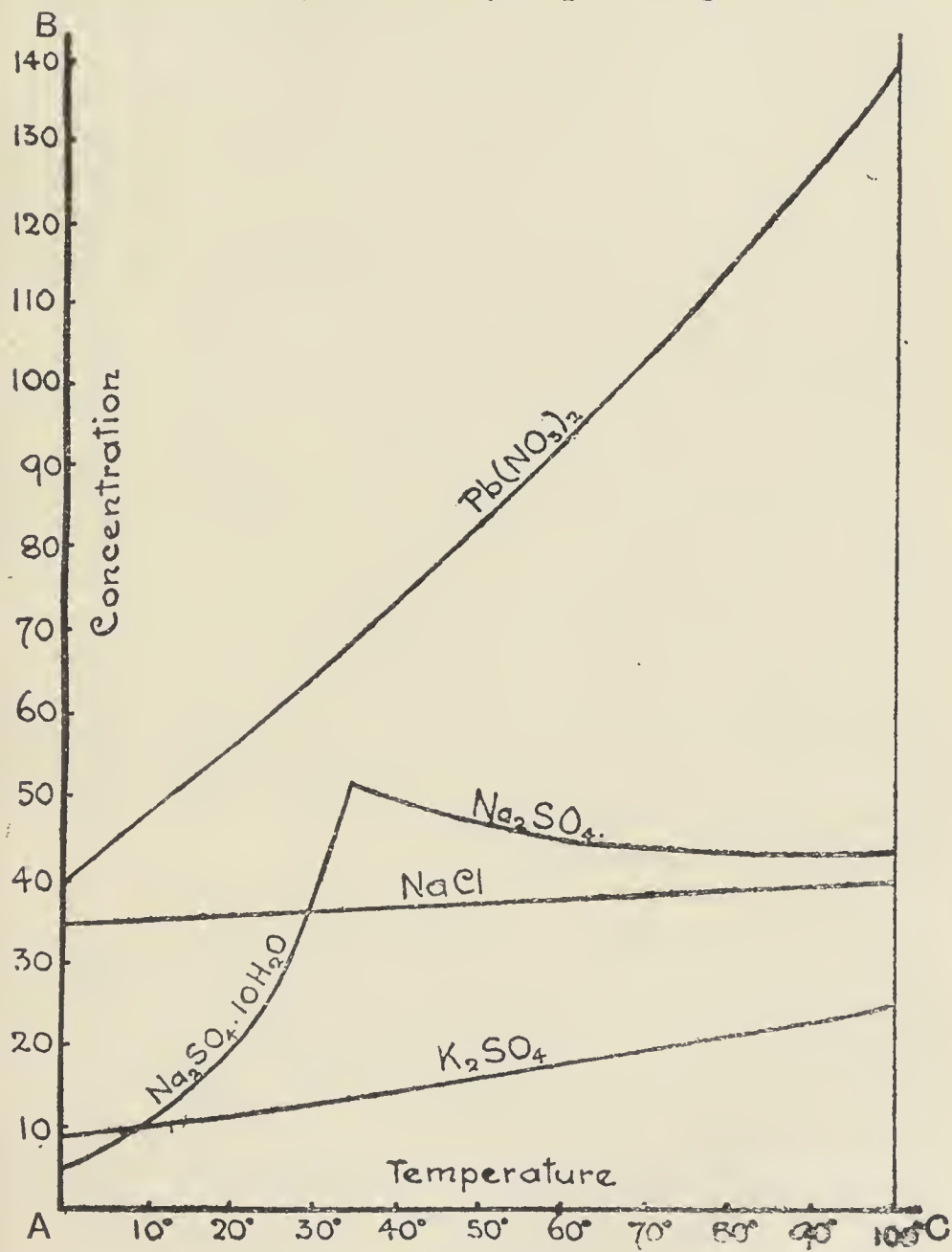

Diagram I.

Section 64), may be stated as follows: If the heat of solution is *negative*, the solubility *increases* with rise of

temperature; and conversely. [In stating this relation, it must be remembered that the heat of solution may vary considerably with the dilution; the quantity referred to above means the heat evolved or absorbed when the substance dissolves in its *nearly saturated solution.*]

The majority of solids dissolve in water with absorption of heat; potassium nitrate and ammonium sulpho-cyanate are familiar examples. [A small quantity of water may easily be frozen if it is brought on the outside of a beaker in which ammonium sulphocyanate is being dissolved.] Caustic potash, anhydrous sodium sulphate and many calcium salts, dissolve with evolution of heat. [Calcium citrate is an example of this and the fact that its solubility is less as the temperature is higher, serves as a test for citric acid in qualitative analysis.]

The influence of *pressure* on the solubility of solids in liquids is very slight, a difference of several atmospheres being required to make a measurable difference in the solubility. Here, again, one may predict the direction in which pressure will affect the solubility by reference to the general law referred to above. This law predicts, and experiment shows, that if the volume *increases* when the solid dissolves (in the nearly saturated solution) an increase of pressure will be accompanied by a *diminution* of solubility: and conversely.

19. Supersaturation. The solubility of a particular solid in a liquid at a given temperature and pressure is perfectly fixed and definite, the solubility being that concentration of the solution at which the solid and solution are in equilibrium. If however the solid is absent, there is no longer any question of this equilibrium; the solution may contain more or less of the solute than the amount it contains when saturated. If it contains more it is said to be *supersaturated* and if it contains less, it is *unsaturated.*

A supersaturated solution at a given temperature is easily made by preparing a saturated, or nearly saturated,

solution at some temperature higher (or in some cases lower; see above) than the given temperature; some temperature, that is, at which it is more soluble. The solution so obtained is now removed from every trace of the solid (e.g., by filtration) and cooled (or warmed) to the given temperature. None of the solid being present this supersaturated solution can remain in an apparently stable condition for a considerable time. But if a trace of the particular solid (generally called a "nucleus") is introduced, crystallisation immediately sets in and the crystals continue to be formed until the remaining solution has the normal saturation strength; equilibrium being thus established between the solid and the solution.

If the degree of supersaturation is considerable, it happens that purely mechanical action (rubbing, shaking, etc.) may cause the crystallisation to take place even though none of the solid is added. According to some authors there is a definite limit of concentration when this happens, that is, there is a concentration beyond which the solution becomes *unstable* or *labile*. Between this limit and the normal saturation concentration the solution is *metastable*. In this case the latter term signifies "stable except in presence of the particular solid."

In bringing about the crystallisation of a supersaturated solution by the addition of the solid, it is found that the merest trace of the solid is sufficient—something like a millionth of a milligram may suffice. But there is a limit to this when the particles approach to what are called "molecular dimensions"; the smaller the particles of the nucleus, the greater must be the degree of the supersaturation in order that crystallisation may be brought about. For the purpose of starting crystallisation in a supersaturated solution of a particular solid, the nucleus added must be either identical with that solid or it may be *isomorphous* with it (see Section 45).

The phenomenon of supersaturation may occur also in other cases of solution, e.g., one may have a supersaturated solution of a gas in a liquid. Very analogous

phenomena are the "superheating" and "supercooling" of liquids; water, for example, may be heated considerably above its normal boiling point, without boiling taking place, if air is carefully excluded. Again, it may be cooled far below its normal freezing point and still remain liquid; in this case, on the addition of a nucleus of solid ice, it starts freezing at once.

Many solids when fused remain liquid, at a temperature far below their melting points, for a considerable time; the addition of a trace of the solid causes immediate solidification. Ordinary glass has in some respects the character of a supercooled liquid and most glasses if kept at a suitable temperature undergo the process known as "devitrification," i.e., they become crystalline.

20. Freezing point and vapour pressure of solutions. A pure liquid has a definite freezing temperature at a given pressure; thus water freezes at $0°$ when the pressure is 760 mm. If the pressure alters, the freezing point alters; but a great difference in pressure usually makes only a very slight difference in the freezing point. *Increase* of pressure *lowers* the freezing point in some substances and *raises* it in others, according as the liquid is denser than the solid or *vice versa*.

A pure liquid also has a definite vapour pressure (or vapour "tension") at a given temperature; thus at $0°$ the vapour pressure of water is 4·6 mm., at $15°$ 12·7 mm. and at $100°$ it is 760 mm. These pressures depend on the temperature only and are quite independent of the quantities of liquid or vapour so long as there is more of the substance present in the vessel than is required to saturate the space with vapour. If we place water in a vessel and completely remove all the air by means of a vacuum pump, there will only be liquid water and its vapour in the vessel; the freezing point of the water is now found to be $+ ·0076°$ instead of $0°$ since, as water at this temperature is more dense than ice, the freezing point is raised by diminished pressure.

Since a liquid boils when its vapour pressure is equal to the superincumbent pressure, it is evident also that a pure liquid has a definite boiling temperature, or boiling point, at a given pressure.

If now we dissolve a substance in a pure liquid, we find that the freezing point, vapour pressure and boiling point are all changed and that their values will all vary continuously as we dissolve more and more of the substance in a given quantity of the liquid; i.e., these properties will vary continuously with the concentration of the solution produced. The *direction* of these variations is as follows: the addition of the solute to the pure liquid *lowers* the freezing point (in nearly all cases; there are some exceptions); *lowers* the vapour pressure and *raises* the boiling point. If we start with a certain quantity of pure water and gradually dissolve common salt in it, the freezing point and vapour pressure of the solution will both diminish continuously as the solution gets more concentrated with salt; but for each concentration of the solution there will be a definite freezing point and a definite vapour pressure at a given temperature. When we have added more salt than is necessary to saturate the solution, so that solid salt, saturated solution and vapour are present, we shall find that, if we keep the temperature constant, the concentration and vapour pressure of the solution have fixed values. If this saturated solution be cooled it will become supersaturated, so that, nuclei being present (see above) solid salt will separate out and the residual solution will become less concentrated than before; but for each temperature there will be a definite concentration (i.e., the solubility of the salt) and a definite vapour pressure.

But if we continue cooling the solution until the temperature is $-22°$ solid ice will begin to separate as well as salt and we shall have solid salt, ice, saturated solution and aqueous vapour together in equilibrium. We shall now find that the strength of the solution is 23·6 grams of salt to 100 grams of water and the vapour

pressure is about 0·7 mm. All the conditions are now absolutely fixed so long as the four "phases"—two solids, solution and vapour—are present. The four phases can only co-exist in equilibrium if the temperature, vapour pressure and concentration of the solution have the definite values mentioned. If any one of these conditions is permanently altered, one or other of the phases will disappear. If we attempt to lower the temperature below − 22°, both ice and solid salt will continue to deposit, the temperature remaining quite constant so long as any liquid remains and only when the whole has solidified will the temperature begin to fall. There is a definite temperature then, at which the liquid solidifies and if we warm the solid so produced, it will melt at this same temperature; moreover, the ratio of water to salt will be the same in the saturated solution and in the solid mixture which separates. Here then we have an example of a mixture which can change its phase without change of composition, i.e., it is "hylotropic." Solid mixtures of this kind were at first mistaken for chemical compounds since they have a fixed melting point and a fixed composition which does not alter on melting; they were called *cryohydrates*. But it is now known that the composition and melting point are only fixed if the pressure is fixed. If we remove the vapour phase (e.g., by putting the mixture into a cylinder fitted with a piston and slightly increasing the pressure) and sufficiently increase the pressure, the temperature of solidification and composition will both be altered. Further, it can be shown that such solids are mixtures by using a coloured solute, such as potassium chromate, when examination of the solid under the microscope will reveal the two distinct sets of crystals, ice and the salt, intimately mixed together.

The temperature at which these mixtures of the *four* phases are in equilibrium is called the *cryohydric point*. If we start with a saturated solution of a salt and cool it, salt separates and the solution left behind becomes

weaker in salt. [We suppose here a salt whose solubility increases with rising temperature.] Conversely, if we cool a very weak solution of a salt, ice separates and the solution becomes *stronger* in salt. These operations will eventually lead to the same result, that is to say, the cryohydric point will be reached in either case and both solids will then separate together.

Examination of the solid which separates when a dilute solution begins to freeze, shows that this solid is, in the majority of cases, the pure solvent only. This can easily be demonstrated by freezing a dilute solution of a coloured solute (e.g. potassium permanganate), when colourless ice separates. Use is made of this fact in concentrating dilute solutions by freezing and removing the ice which first separates. But many cases are known in which the separated solid proves to be a mixture of solid and solute; in these cases the freezing point is not lowered as much as it would be if only pure solid solvent separated. In fact there are instances in which proportion of solute in the separated solid may be greater than in the solution and the residual solution may therefore become *weaker* instead of *stronger*.

21. Solutions of liquids in liquids. The solubility of liquids in one another shows very great variation according to the nature of the liquids. Mercury and water, for example, are to all intents and purposes absolutely insoluble in one another, at any rate as far as practical tests can show; ether and water dissolve one another to a limited extent, so that, unless the proportions are very different the mixture separates into two layers; whilst alcohol and water dissolve one another in all proportions. It is usual therefore to classify the solutions of liquids in liquids under three heads, namely those which are (1) non-miscible, (2) partially miscible and (3) miscible in all proportions. It must be noted however first, that probably all liquids do dissolve in one another to some extent, but the quantity dissolved may be too

small to be detected; and secondly, it must be remembered that liquids which are only partially miscible at one temperature may become completely miscible at another temperature. Still the classification is an extremely useful one and we will proceed to consider, briefly, the three cases.

Non-miscible liquids. In a mixture of two non-miscible liquids, each constituent behaves as if the other were absent, so that the vapour pressure of the mixture is the sum of the vapour pressures of its constituents. The mixture will boil, in an open vessel, when the sum of the vapour pressures is equal to the atmospheric pressure. If such a mixture is distilled, the volumes of the two vapours which pass over will be in proportion to their vapour pressures, at the temperature employed, and the quantities by weight of each which passes over will therefore be proportional to the vapour pressure multiplied by the vapour density. This principle has been made use of in determining vapour densities, since, if we find the ratio of the quantities which distil over and if we know the vapour density and vapour pressure of one of the liquids, we can calculate the vapour density of the other liquid. The process of "steam distillation" of high boiling point liquids depends on this principle; the effect is equivalent to distilling under reduced pressure at the same temperature.

22. Partially miscible liquids. When ether is shaken up with a very small proportion of water, complete solution results; we obtain what we call a solution of water in ether. Similarly, if we shake up a very little ether with plenty of water, we again get a complete solution which we call a solution of ether in water. [As stated above, it is customary to call the component which is in excess the solvent and the one present in smaller amount the substance dissolved or solute.] But if we shake up ether and water in quantities which are not greatly different, the mixture will separate into two layers, or two "phases." The lower layer will be a

solution of ether in water, the upper one will be a solution of water in ether and each of these solutions will be saturated. There is evidently, for each pair of partially miscible liquids, a definite concentration of one in the other beyond which the mixture will separate into two layers. But this refers only to one particular temperature. If the temperature alters, the solubilities alter; the solubilities may either increase or diminish, as the temperature rises, according to the nature of the liquids. Suppose a case in which the solubilities both increase as the temperature rises; then, the pair of liquids which were only partially miscible at one temperature may become completely miscible at a higher temperature. This is the case with phenol and water. Water will dissolve about 8 per cent. of phenol at the ordinary temperature; if more phenol is added, the mixture will separate into two layers. But on raising the temperature complete solution again results and more phenol must be added in order to produce two layers. We can go on doing this continuously up to a certain definite temperature—68·4° in this case—but beyond this, we can never get two layers, no matter how much phenol we may add. Similar behaviour will be noticed if we add water to phenol. There is a temperature then above which phenol and water always form a homogeneous liquid no matter what are the proportions; below this temperature two layers can always be obtained if sufficient excess of one or other liquid is added. This temperature is called the *critical solution temperature* and the concentration of the solution at this temperature is called the *critical concentration*.

In some pairs of partially miscible liquids, the solubilities may diminish as temperature rises; in this case the liquid becomes homogeneous *below* the critical solution temperature and may be caused to separate into two layers *above* this temperature when sufficient excess of one or other constituent is added. An instance of this is triethylamine and water.

The vapour pressure of a mixture of two partially miscible liquids is always *less* than the sum of the vapour pressures of the two, since the vapour pressure of each liquid is lowered by the solution in it of the other. [Compare page 75.] But as long as *two layers are present* the vapour pressure of the mixture is *constant* and the concentrations of the solutions are also constant, for a given temperature. This is true no matter in what proportions the two liquids are mixed so long as the two liquid phases are present.

23. Completely miscible liquids. When the two liquids dissolve one another in all proportions, giving a homogeneous mixture, the properties of the mixture will continuously alter as we add one or other constituent. In the case of partially miscible liquids, we saw that the vapour pressure and concentrations of the solutions remained constant, at a given temperature, no matter how much of one or other liquid we added, provided two layers were present. In the case of the homogeneous mixture, the vapour pressure and composition can be continuously varied, although the temperature is kept constant. For each value of the concentration however there will be a definite vapour pressure at a given temperature.

The vapour pressure of a homogeneous mixture of two liquids is never as great as the sum of the two vapour pressures of the two liquids separately. It may (*a*) lie evenly between the two, (*b*) reach a maximum at a certain concentration, or (*c*) reach a minimum at a certain concentration. Examples will make this statement more clear.

(*a*) At a given temperature methyl alcohol has a higher vapour pressure than pure water. If now we gradually add methyl alcohol to water, the vapour pressure will continuously rise; if we add water to methyl alcohol the vapour pressure will continuously fall. Since mixtures richer in methyl alcohol have a higher vapour

pressure, it is evident that, on submitting a mixture of methyl alcohol and water to distillation, the composition of the vapour will be different from that of the residual solution. Mixtures richer in methyl alcohol will tend to come over first and the composition and boiling point of the residual solution will continuously alter as distillation proceeds. If we collect the first portion of the distillate and submit this again to distillation, we shall again get a richer mixture coming over first, and, by repeating this process often enough, we may effect a nearly complete separation of the two constituents (fractional distillation).

(b) A mixture of propyl alcohol and water containing about 75 per cent. of propyl alcohol is found to have a higher vapour pressure, at a given temperature, than a mixture of these two constituents in any other proportion. Consequently, on distillation of any mixture of these two substances, the portion which first comes over will approximate in composition to this. If, for example, a mixture containing 50 per cent. of each constituent is distilled, a distillate richer in propyl alcohol is obtained, which, on repeated distillation, yields the mixture of *maximum* vapour pressure or *lowest* boiling point containing 75 per cent. of the alcohol. The residue left in the retort is therefore richer in water, i.e., poorer in propyl alcohol. If a mixture containing 90 per cent. of propyl alcohol is distilled, the 75 per cent. mixture tends to come over first, as in the previous case, leaving a mixture behind in the retort which is richer in propyl alcohol and poorer in water.

If now we start with the 75 per cent. mixture and submit it to distillation, it boils at a *constant temperature* and comes over as a whole, i.e., *unchanged in composition*.

(c) Mixtures of water with nitric acid, hydrochloric acid, formic acid or hydrofluoric acid, behave in the opposite way to the mixture of water and propyl alcohol. That is to say, a mixture having a certain concentration, will have a lower vapour pressure, or higher boiling point,

than any other mixture.   Thus it is found that a mixture
of hydrochloric acid and water which contains about
20 per cent. of hydrochloric acid has a lower vapour
pressure, at a given temperature, than any other mixture
of these two substances.   Consequently, on distilling a
stronger solution, mixtures richer in hydrochloric acid
will first pass over; whilst if a weaker solution is distilled,
mixtures weaker in acid will come over first.   In either
case the mixture which comes over last is the 20 per cent.
solution, which has the lowest vapour pressure.

Constant boiling point mixtures.   In the two types of
mixtures (*b* and *c*) last mentioned, we see that there is
in each case a mixture of a certain concentration which
has a constant boiling point and which can be distilled
without change of composition.   Such mixtures are there-
fore "hylotropic" substances, i.e., they change their
phase without change of composition.   For this reason
they were formerly regarded as chemical compounds,
since constancy of composition and a fixed boiling point
were regarded as characteristics distinguishing chemical
compounds from mixtures.   A most important point,
however, had been overlooked, namely, that the com-
position and boiling point of such mixtures alter con-
tinuously with *pressure*.   If we considerably alter the
pressure, we shall still obtain a constant boiling mixture
when the composition reaches a certain value; but the
composition and boiling point will now be different from
their former values.   Thus, at a pressure of 760 mm.,
the constant boiling mixture of hydrochloric acid and
water contains 20·24 per cent. of the acid; at 50 mm. it
contains 23·2 per cent. and at 1800 mm. 18 per cent.

It is evident therefore that a mixture of these sub-
stances of a given composition is only hylotropic at *one
particular temperature and pressure*.   A chemical compound,
on the other hand, has a fixed composition, and may
change its phase without change of composition at various
temperatures and pressures.   We can boil a volatile
liquid chemical compound at any temperature, within

certain limits, if we suitably adjust the pressure, or at various pressures, if we suitably adjust the temperature; and the composition remains unchanged under all these changes of condition.

The constant freezing mixtures or "cryohydrates" referred to in a previous section are closely analogous to these constant boiling mixtures. In neither case should the composition and properties be referred to as "constant," unless the particular pressure is stated.

24. Solutions of gases in liquids. It is probable that every liquid can dissolve every gas; but the solubilities may differ enormously according to the nature of the gas and liquid. Thus, one volume of water at 0° dissolves about 0·02 volume of hydrogen, 1·8 of carbon dioxide, 4·3 of hydrogen sulphide, 80 of sulphur dioxide and 800 of ammonia. Gases which are easily liquefied are usually the most soluble. The solubility of a gas in a liquid is generally expressed in terms of volume (unless the gas is extremely soluble when it is sometimes more convenient to refer to the mass dissolved). Thus, the solubility of a gas at a given temperature is now usually defined as the volume of the gas which can be dissolved by unit volume of the liquid at that temperature. If V vols. of liquid dissolve v vols. of gas, the solubility is $\dfrac{v}{V}$. [Note that the "coefficient of absorption," a term employed by Bunsen, is not quite the same thing; its value is $\dfrac{v}{V(1 + \alpha t)}$.] The solubility of all gases in liquids diminishes as the temperature is higher*. As might be expected therefore from what was said above (page 37), all gases dissolve in liquids with evolution of heat. Exceptions have been stated to exist, but these are very doubtful.

The most important law which regulates the solution of gases in liquids is known as Henry's law. It states

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* Helium, within a certain range of temperature, is said to be an exception.

that, at a given temperature, *the mass of gas dissolved by a given quantity of a liquid is directly proportional to the pressure.* Thus if at a pressure of one atmosphere, one volume of water dissolves w grams of a gas, then at two atmospheres it will dissolve $2w$ grams, and at three atmospheres $3w$ grams, and so on. But according to Boyle's law, the volume of a gas varies inversely as the pressure; therefore the *volume* dissolved is always the same: i.e., it is independent of the pressure. If a *mixture* of gases is shaken up with a liquid, each gas will dissolve in proportion to its *partial pressure* (Dalton's law) and in proportion, also, to its solubility. Thus the solubilities of oxygen and nitrogen at 0° are about 0·04 and 0·02 respectively, and if we shake up atmospheric air with a little water at 0° and 760 mm. the relative quantities of the two gases dissolved will be approximately as $0·04 \times \frac{1}{5}$ of 760 : $0·02 \times \frac{4}{5}$ of 760, since the volumes are about 1 : 4.

Henry's law is found to hold well for the less soluble gases at the ordinary temperature and pressure, but the very soluble gases show deviations. Thus ammonia obeys the law only above about 100° and sulphur dioxide above about 40°.

Carbon dioxide, in dissolving in water, obeys the law at ordinary temperature and pressure, but at high pressures and low temperatures it becomes less soluble than it ought to be in accordance with the law. If c is the concentration of the gas in the liquid and P is the pressure, Henry's law states that $\dfrac{P}{c}$ will be constant; with carbon dioxide however, this ratio slightly but continuously increases as the pressure increases.

Deviations from Henry's law are often explained by assuming that chemical change takes place and this explanation may, in certain cases, be the correct one. If a part of the gas on dissolving changes partly into another substance or substances, it is only the *unchanged* part which is in equilibrium with the gas outside. But there is another way in which many of these exceptional

cases may be explained; namely, that the substance has not the same molecular weight in the gas state as it has in solution. This explanation will be more fully considered below. In the case of carbon dioxide, for example, this result could be explained if we assume that the substance is C_2O_4 in the highly compressed gas and CO_2 in the solution.

Determination of the solubility of gases in liquids. In the case of the less soluble gases the most usual method is to shake a known volume of the liquid with excess of the gas in a graduated tube over mercury and measure the diminution of volume which occurs in the gas. If the gas is very soluble in the liquid, ammonia in water, for example, this method would obviously be unsuitable; in such cases a saturated solution of the gas in the liquid is prepared and a weighed quantity of this saturated solution is analysed, the process being quite analogous to that employed in determining the solubility of solids. The less soluble gases can also be determined in a similar way. Thus we can measure the solubility of carbon dioxide by preparing a saturated solution of it and estimating the amount of the gas dissolved by means of baryta water.

25. The Partition law or Distribution law. When a substance is shaken up with two solvents which are themselves non-miscible, or nearly so, it will dissolve in both of them; but the quantities taken up by a given volume of each solvent may, of course, be very different, according to the solubility of the substance in each. If we measure the concentration (i.e., the quantity of the substance in unit volume) of the substance in each solution we shall find that, at a given temperature,

$$\frac{\text{concentration in one solution}}{\text{concentration in the other solution}} = \text{a constant.}$$

This ratio is called the *partition coefficient* or *distribution ratio*.

If we take varying quantities of one or other liquid, or of the dissolved substance, the actual concentration in each liquid will, of course, be different; but the *ratio* remains the same, no matter what quantities we take. For example, if we shake up iodine with carbon disulphide and water in any proportions, at 15°, we shall find that the concentration of the iodine in the carbon disulphide solution divided by its concentration in the water solution is always 410, no matter what quantities we used.

With solvents which are partially miscible, like ether and water, the law is, of course, less exact, since the solubilities of ether in water and water in ether vary with the quantity and nature of substances dissolved in them. But sufficiently good results may be obtained with ether and water within certain limits.

This important law is quite general for all cases in which a substance dissolves, or distributes itself, between two non-miscible phases which are in contact. Henry's law, for the solubility of gases in liquids, may be regarded as an example; this law states that the concentration c_1 of the gas in the solution is directly proportional to the pressure, P, of the gas, or $\frac{c_1}{P}$ is constant. But the pressure of the gas is of course proportional to its concentration, c_2. Therefore we may write, $\frac{c_1}{c_2} =$ a constant; that is to say, the quantity contained in unit volume of the gas space is directly proportional to the quantity contained in unit volume of the solution.

There are many cases in which this simple partition law does not hold. If, for example, we shake up an aqueous solution of succinic acid with ether, we find that the law holds; if c_1 is the concentration of the acid in the water and c_2 that in the ether, $\frac{c_1}{c_2}$ is constant no matter how we alter the quantities. But on making a similar experiment with benzoic acid in water and benzene

we find that we get different values of $\frac{c_1}{c_2}$ for different quantities taken. Here it is found that in order to get constant numbers we must take the ratio of the concentration in the water to the *square root* of the concentration in the benzene. Now it can be shown, by methods which will be described later, that succinic acid has the same molecular weight in ether solution as it has in water solution, whereas benzoic acid has the normal molecular weight in water solution, but approximately *double* this molecular weight in benzene solution, i.e., most of the molecules of benzoic acid in the benzene are "associated."

A large number of similar cases have been investigated and the results, which can be completely explained in a theoretical way, may be generally stated as follows:

If the substance has a normal molecular weight in phase A and a molecular weight n times as great in phase B, the concentration of the substance in A is proportional to the nth root of its concentration in B—

or $\frac{c_1}{\sqrt[n]{c_2}} = K$. K is a constant depending on the nature of the substances and on the temperature. If therefore we know the molecular weight of a substance in one phase and if we determine K experimentally, we can calculate the molecular weight in the other phase.

26. Solutions of gases in solids. A gas may be taken up by a solid in a variety of ways, of which the following may be regarded as typical. It may

I.   Unite with the solid forming a *chemical compound*.

II.   Dissolve physically in the solid forming a homogeneous *solution* of continuously variable composition.

III.   Adhere more or less firmly to the *surface* of the solid only, without entering into the interior; this phenomenon is called *adsorption* of the gas.

But in many cases these typical phenomena may occur simultaneously, or one may follow the other. Physical solution may first occur at low pressure and when the

pressure reaches a certain value chemical combination may take place. Or, the gas may first be adsorbed on the surface and then diffuse into the interior forming a solution; it has been proposed to call this phenomenon *sorption*.

These phenomena, which are of great importance in chemistry, may be investigated in several different ways. The most direct experimental method consists in ascertaining the relation which exists between the pressure of the gas and the concentration of the gas in the solid, when equilibrium is established. [The quantity of the gas which is taken up by a given quantity of the solid is referred to here as its concentration, whether it actually enters the solid or not.] In order to carry out an experiment of this kind a given quantity of the solid is placed in a small flask or tube connected with a manometer. The apparatus is first rendered vacuous and the gas is then allowed to enter, through a stopcock, in such a way that its quantity can be varied at will, i.e., it can be pumped in or sucked out. The stopcock is then closed, the temperature kept constant and the pressure is observed on the manometer when it becomes constant.

In the three typical cases mentioned above, the following facts may be observed:

1. If the solid unites chemically with the gas, the pressure will remain perfectly *constant* for a *given temperature*. If we now pump out some of the gas, the pressure will, of course, temporally, sink; but after closing the stopcock and allowing the system to come to equilibrium, the pressure will go up again and will eventually reach its former value. Or, if we pump in more gas, the pressure will at first rise, but after closing the communication it will sink again to its original value. The same results will be obtained, within certain limits, no matter what quantities of gas or solid are present. These facts may be shortly expressed by saying that the pressure is a *function of the temperature* only and is *independent of the quantities*. This statement is generally

referred to as Deville's law of dissociation. In most cases this law holds for a considerable range of pressures; there are limits however, for if we pump out nearly all the gas, or pump in a large excess of gas, the pressure no longer remains constant but increases or diminishes as more gas is pumped in or sucked out. At the lower limit the compound is all dissociated and at the higher limit all the original solid has been converted into chemical compound; in order that the pressure shall remain constant independently of the quantities, it is necessary that the original solid, the chemical compound and the gas shall all three be present.

2. If the gas dissolves physically in the solid, as a solid solution, the concentration of the gas in the solid will vary continuously as the pressure is altered. Three cases present themselves: (a) If the molecular weight of the substance is the same in the two phases, i.e., if the gas does not change in molecular state in dissolving, Henry's law will be obeyed, that is to say, the concentration in the solid will be directly proportional to the pressure, or $\dfrac{P}{c} = K$.

(b) If however the molecular weight in the solid phase is n times as great as it is in the gas phase, i.e., if the gas undergoes association when dissolved, the relation will be $\dfrac{P}{\sqrt[n]{c}} = K$.

(c) The substance may have a simpler molecular formula in the solid phase than in the gas phase, i.e., it may undergo dissociation in dissolving in the solid. In this case the relation will be $\dfrac{\sqrt[n]{P}}{c} = K$.

3. If we know, from molecular weight determination, that the substance in the gas phase is present in single molecules and that when it dissolves in the solid the relation is $\dfrac{P}{\sqrt[n]{c}} = K$, we can always explain the result by

saying that association has occurred in the solid phase. Similarly, if the ratio is found to be $\frac{\sqrt[n]{P}}{c} = K$, we may in many cases conclude that dissociation has taken place. Thus when hydrogen dissolves in palladium at low pressures, the relation appears to be $\frac{\sqrt{P}}{c} = K$ and from this it has been concluded that the gas dissolves in the solid as single atoms, since we know that it is H_2 in the gas. But there are numerous instances in which this explanation is inadmissible. Thus hydrogen when taken up by charcoal, under certain conditions, gives the relation $\frac{\sqrt[3]{P}}{c} = K$, and since hydrogen in the gas state is known to be diatomic we should have to assume that it dissolved in charcoal in fractions of atoms, which is absurd. In all such cases, i.e., those in which the solid solution theory would lead to absurd results, it is the custom to make the assumption that the gas is held on the *surface* only and is not dissolved. This phenomenon is known as *adsorption*, a term originally introduced by du Bois Raymond.

Solids take up substances from solutions just as they take up gases and the phenomena are analogous in every way. Most of the experiments on adsorption have been carried out with porous solids and substances dissolved in water or other solvent.

27. The *law of adsorption* is usually stated in the following way. Suppose a quantity of a porous solid, whose surface is S, is kept in a solution of a substance until equilibrium is attained, a certain quantity Q of the dissolved substance will be adsorbed on the surface of the solid; if C is the final concentration of the solution, the relation will have the form

$$\frac{Q}{S} = KC^n,$$

where K is a constant depending on the nature of the substances and n is a number which is, as a rule, *less* than unity. The solid is sometimes called the *absorbens* and the dissolved substance the

absorbendum. Adsorption may be either positive or negative, that is the introduction of the porous solid may either weaken or strengthen the solution; the former is by far the more common.

28. Solutions of solids in solids. When two solids are melted together, or dissolved together in a solvent, it happens in some cases that, on solidifying the molten liquid, or allowing the solution to crystallise, the solid which separates is a uniform homogeneous mixture of the two solids whose composition is continuously variable. The properties of this homogeneous mixture, such as the melting point and density, are also continuously variable with the composition. Such solid homogeneous mixtures are called solid solutions.

As in the case of liquid solutions, we may have solids which are miscible with one another in all proportions; as examples of this may be mentioned isomorphous substances such as the alums; we can obtain homogeneous crystals of common alum and chrome alum containing any proportion of the constituents. Similarly with many pairs of metals such as gold and platinum or copper and nickel.

Again, we may have partial miscibility in solids. We have examples of this in iron and carbon or sodium chlorate and silver chlorate; these can form homogeneous solid solutions of continuously variable composition, but only within certain limits.

Probably most of the laws relating to the properties of dilute liquid solutions are applicable also to dilute solid solutions, but the study of the latter has not gone very far. Van't Hoff showed that in certain cases the solid which separates on freezing a solution does not consist of the pure solid solvent, but a homogeneous mixture of solvent and solute of continuously variable composition (compare page 42). He found that the concentrations of the dissolved substance in the separated solid and in the liquid bear a constant ratio to one another. A similar relation may also exist in certain cases between the concentrations of a substance in the

gaseous state and in a solid in contact with it, as shown above; it is evident therefore that the partition law is applicable to solid solutions. That diffusion can take place of one solid into another was proved by Roberts-Austen, who showed that metallic gold can diffuse into a cylinder of lead, placed in contact with it, at the ordinary temperature.

It may be observed that the above definition of "solid solution" would include glass, sealing wax and other non-crystalline homogeneous substances which have a continuously variable composition. There are many important differences however between crystalline and amorphous solids, and some authors are disposed to regard only the former as true solids and the latter as belonging rather to the class of supercooled liquids.

29. Disperse Systems. Many instances will be familiar to the student, of systems, consisting of two phases, in which one of the phases is continuous and the other is distributed throughout it in the form of small particles. Fine clay suspended in water, oil shaken up vigorously with water, milk, smoke, dust and foam are all examples. These are called disperse systems. The phase which is continuous is called the *dispersion medium* and that which is distributed through it is called the *disperse phase*. If the dispersion medium is a liquid and the disperse phase is a solid, the system is called simply a *suspension*; whereas if the medium is a liquid and the disperse phase is also liquid, the system is an *emulsion*. These disperse systems have many peculiar properties; they remain for a considerable time without apparent alteration, but, as a matter of fact, they are in most cases slowly but continually changing; the small particles tend to aggregate together into larger particles and when these reach a certain size they settle under the action of gravity or, in case of liquids, separate into drops or layers. The addition of foreign substances will often accelerate this change, this influence being most marked in the case of salts, acids and bases. The stability of these systems depends upon various factors, but most noticeable is the influence of the average size of the particles; as the size of the particles diminishes the system becomes more stable. This fact is intimately connected with the circumstance that as the particles become smaller the relative surface exposed is greater. Thus, a centimetre cube of a solid exposes 6 square centimetres, but if divided symmetrically into 1000 milli-metre cubes, the surface exposed will be 60 square centimetres,

and so on. In the case of a suspension of clay in water one can see most of the particles with a lens. In finer suspensions a microscope is necessary. There are other cases in which even a microscope reveals nothing, yet the presence of dispersed particles can be made evident by passing a beam of light into the liquid, when a milkiness or glow appears, the light from which is found to be polarised (Tyndall effect). By using a very bright light and observing this effect under a powerful microscope, the presence of extremely minute particles can be demonstrated (ultramicroscope). The possibility of demonstrating the presence of fine particles in a medium depends to some extent on the refractive and dispersive powers of the two phases. If these are sufficiently different, particles whose diameter is not less than 0·1 mm. can be recognised by the eye, and those whose diameter is not less than about 0·00015 mm. can be detected by a powerful microscope. But with the aid of the ultramicroscope it is possible to make evident the presence of particles of about five millionths of a millimetre in diameter.

The stability and the general character of these disperse systems vary considerably according to the size of the particles, but the variation is quite gradual. It is convenient however to divide them into three classes according to the average size of the particles: (1) if the diameter of the particles is greater than $\frac{1}{10000}$ mm. the system is called a coarse *suspension* or coarse *emulsion*; (2) if it is between $\frac{1}{10000}$ mm. and one millionth of a millimetre it is called a *colloidal solution*; (3) although we have no means of practically demonstrating particles below this limit, there is every probability that smaller particles do exist and that what we call *true solutions* may in reality be heterogeneous.

Colloidal solutions. According to this view, colloidal solutions occupy an intermediate position between coarse suspensions, or emulsions, and true solutions, but there is no sharp line of demarcation between the classes. For a long time colloidal solutions were regarded as homogeneous solutions, but the presence of disperse particles has been clearly proved in most of them. In the earlier observations the majority of the substances which were found to give colloidal solutions were found to have certain general characters, e.g. (1) they diffuse with extreme slowness, (2) they are practically unable to pass through animal membranes or through parchment paper, (3) they are non-crystalline, and (4) they often appear to have complex chemical formulae. They were therefore regarded as a distinct family, *substances* being classed as crystalloids and colloids. Recent work has shown, however, that probably all solid substances can be made to exist in either state—i.e. one and the same chemical individual can exist either in the crystalline state or the colloidal state. It would appear then, that we should not speak of any given *substance* as a colloid or a crystalloid; the terms should refer to the *state* of matter.

Colloidal solutions may be further classified according to their general characters as *suspensoids* and *emulsoids*, these names being given from the close resemblance with suspensions and emulsions respectively.

The suspensoids as a class show the following characteristics: (*a*) their solutions are not more viscous than water, (*b*) they are coagulated or precipitated by very minute quantities of salts, acids or bases, (*c*) the precipitates obtained from them are usually powders or amorphous masses, (*d*) the solutions have, as a rule, no appreciable osmotic pressure (see Section 34).

Emulsoid colloids (*a*) give viscous solutions, (*b*) can be coagulated or precipitated by salts only if the salt is added in very large excess, (*c*) the precipitates are gelatinous or the whole may set to a jelly, (*d*) many of them give, in solution, measurable osmotic pressures.

The suspensoid colloidal solutions are undoubtedly solid-liquid systems and the emulsoid colloidal solutions are, probably, liquid-liquid systems. Most of the best known examples of suspensoid colloids happen to be inorganic substances (e.g. colloidal platinum, gold and silver, colloidal arsenious sulphide), whilst most of the commoner emulsoid colloids are organic (e.g. gelatine, albumen, starch); hence the older and somewhat inaccurate names "inorganic" and "organic" colloids. The names "hydrophobe" and "hydrophile" colloids are also sometimes used for these two classes.

30. Two more important characteristics of disperse systems must be briefly referred to here.

(1) The disperse particles, in nearly all cases, appear to be *electrically charged*. If the terminals of a powerful battery are immersed in the system the disperse particles will move towards one of the electrodes and will tend to aggregate there. In most of the systems examined the particles travel towards the anode and are referred to as "negative colloids." In colloidal ferric hydroxide and some others the particles move towards the cathode and these are termed "positive colloids." The phenomenon is spoken of as *electrophoresis* or as anaphoresis and cataphoresis respectively.

In the case of albumen, and some other substances, it has been found possible to cause the particles to move either towards the cathode or anode by addition of acid or alkali. Further, by careful adjustment a neutral or "iso-electric" point may be reached at which the particles do not show a tendency to move either way. At this point the colloidal solution appears to have a minimum stability.

(2) In all disperse systems in which the disperse particles are not greater than about 0·01 mm. in diameter it is found that the particles are in more or less active *motion*, which is quite continuous (Brownian movements). The rapidity and character of the motion depend on the viscosity of the medium and on the size of the particles. With larger particles and more viscous liquids the motion

is sluggish and more or less rotatory, whereas with the smaller particles in less viscous media it is extremely lively and zig-zag in character.

There appears to be no doubt that these movements are produced by the impacts of the moving molecules of the liquid on the disperse particles, i.e. the Brownian movements actually indicate the motion of liquid molecules and afford confirmation of the kinetic theory.

31. Alloys. When two metals are melted together there may result (*a*) complete miscibility, (*b*) partial miscibility, or (*c*) non-miscibility. Thus lead and silver, gold and platinum, copper and zinc and many other pairs of metals appear to mix together in the liquid state in all proportions. Lead and zinc however only mix slightly with one another; if we melt the two metals together we obtain two layers, the upper one being zinc containing a little lead and the lower one lead containing a little zinc. Aluminium and lead are practically non-miscible at temperatures near their melting points. The cases are quite analogous therefore to those which were considered under the section dealing with solutions of liquids in liquids. Compare, for example, alcohol and water, phenol and water, and mercury and water. [As previously stated, it is probable that absolute non-miscibility does not exist; also it is probable that there may be a "critical solution temperature" at which the partially miscible metallic liquids would become completely miscible.]

If then we melt two or more metals together and cool the mixture until it completely solidifies, we may in certain cases obtain two distinct solid layers which can easily be mechanically separated from one another. But more usually we obtain a solid which has a uniform composition, although it need not necessarily be homogeneous. That is to say, the metals have become intimately associated together. Such an intimate "association" of two or more metals is called an *alloy*. Alloys however may belong to distinct types which have very different characters and we will attempt here to give a

very brief outline of the essential characters of the principal types and to indicate the methods by which they may be recognised, confining ourselves to the simpler cases and considering the alloys of two metals only.

I. *Eutectiferous alloys or conglomerates.* Alloys of this type are *heterogeneous* mixtures of the two metals. Although they appear homogeneous to the eye, it is generally possible to distinguish the distinct crystals of the two component metals if the alloy is examined microscopically under suitable conditions.

II. *Chemical compounds.* Many metals combine together chemically; the resulting compound, if pure, has then specific properties, its composition bears some simple relation to the atomic weights of the metals, and the alloy is, of course, *homogeneous.*

III. *Solid solutions or isomorphous mixtures.* Alloys of this type are *homogeneous* and their composition is continuously variable, at any rate within certain limits.

In addition to these simple types, we may have alloys which consist of a chemical compound *plus* one or other of its constituents, a chemical compound mixed with a solid solution, a mixture of two solid solutions and so on.

32. In order to recognise the character of an alloy and to classify it, if possible, under one of the above heads, various methods are employed. Three methods will be mentioned here which have been most extensively used.

(a) *Optical methods.* The alloy is first cut in sections, polished, "etched" with a suitable reagent, such as cupric chloride, ferric chloride or aqua regia, and then examined under the microscope. In the case of alloys of the first type, it is then usually possible to distinguish the presence of the two constituents, i.e. to establish the fact that the alloy is heterogeneous. In certain cases where this treatment fails to give satisfactory indications, use has been made of X-rays (see Section 103); the alloy may in this way be examined by transmitted radiation, and if the transmitted rays are then allowed to fall on a photographic plate, the resulting photograph will reveal the presence of the two constituents, if one is more opaque to the rays than another.

(b) *Freezing point determinations.* An alloy of the first type (*conglomerate*) of two metals, A and B, when fused, may be looked upon as a solution of A in B or of B in A. If we start with a fused

alloy containing a little B dissolved in an excess of A and cool it down until it just begins to solidify the solid which separates will be the pure metal A (see page 43).   If we remove the part which has solidified, it is evident that the liquid alloy remaining is richer in B than the original alloy was; it will therefore have a lower freezing point.   We may continue this process, getting liquids richer and richer in B and having lower and lower freezing points.   Conversely, if we start with a fused alloy of a little A in an excess of B, the solid which first separates on cooling will be pure B and the residual liquid will be richer in A.   Continually removing the solid B which separates we get liquids richer and richer in A.   Starting in either way then it is evident that we shall eventually reach a certain strength of the solution, i.e. a certain concentration of A in B or B in A, such that, on further cooling, both A and B will separate together.   The temperature at which this happens will remain perfectly constant as long as the liquid alloy is present in contact with the *two* metals, even though we continue to withdraw heat from the mixture.   Further, the composition of the solid mixture which separates will be the same as that of the liquid alloy in contact with it.   Diagram II illustrates an example.

The mixture of metals which thus separates is called the *eutectic* alloy of the two metals and the temperature at which it solidifies is called the *eutectic point*.   The phenomena described here are quite analogous to those referred to on page 41 which take place on cooling down a strong and a weak solution of a salt; the cryohydric point being entirely similar to the eutectic point.   Because of the constancy of composition and fixed freezing point, eutectic alloys were at first regarded as chemical compounds, just as cryohydrates were; the proofs that they are mixtures and not compounds are of the same kind in both cases.
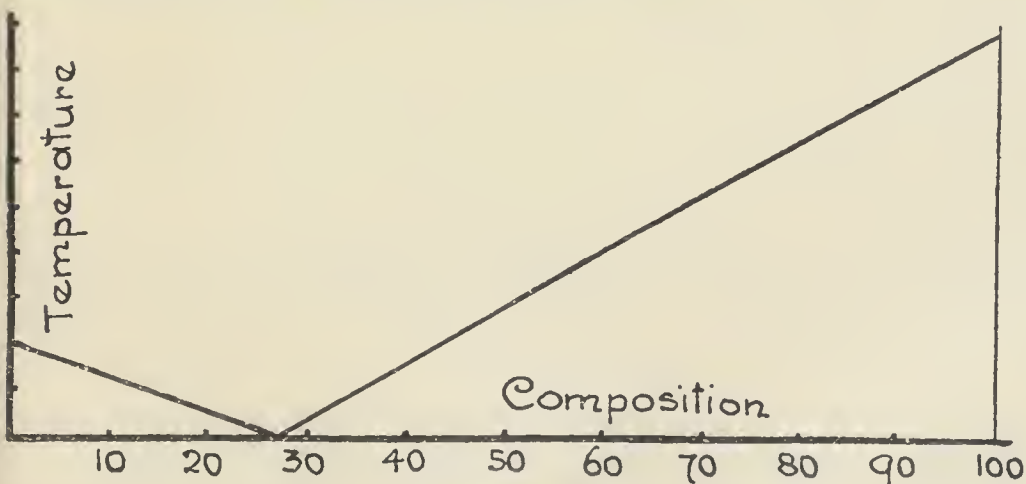

Diagram II.

An alloy which is a pure *chemical compound* will, when fused, behave on cooling just like a single metal; that is, it will have a definite fixed freezing point and the composition of the solid which separates will be the same as that of the liquid which remains. [If we greatly alter the pressure the freezing point will, as a rule, alter slightly, but the composition remains the same as before, both of the liquid and solid.] If, on the other hand, we start with an alloy which consists of a chemical compound of two metals, *A* and *B, plus* an excess of one of its constituents, it may behave, when melted and cooled, just like a conglomerate. If there is an excess of *A*, the crystals which first separate on cooling will be pure *A* and the solution will be richer in the chemical compound *AB*. Conversely, if we start with an alloy of *AB plus* excess of *B* the solid separating will be pure *B* and the residual solution will be stronger in *AB*. Or, if the initial alloy is a mixture of *A* with excess of *AB*, or of *B* with excess of *AB*, the solid which first separates on cooling will be the pure compound *AB*. Evidently then, a series of alloys of the compound *AB* with varying quantities of one or other constituent, will have a *maximum* freezing point when the proportion of the constituents are those exactly corresponding to the composition of the chemical compound, i.e. where neither *A* nor *B* is in excess. For such alloys, there will be *two* eutectic points; one of these will correspond to the eutectic (lowest melting) mixture of *AB* with *A* and the other to the eutectic mixture of *AB* with *B*. An example is illustrated in the following Diagram.
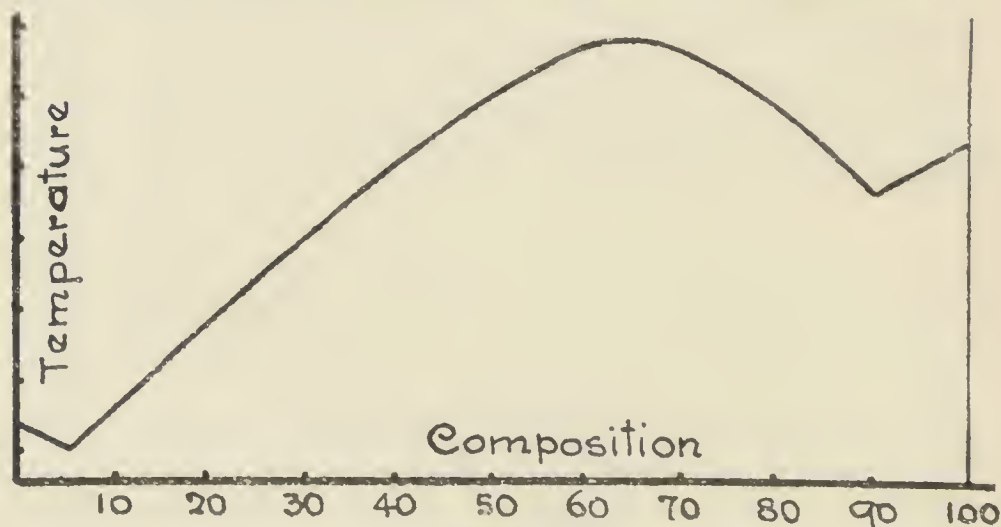

Diagram III.

In the case of alloys which belong to the third type (*solid solutions*, or *isomorphous mixtures*), the solid which separates on cooling the fused alloy will, unlike the two cases considered above,

always contain *both* metals and the residual solution may be either *weaker* or *stronger* than the original solution according to the composition of the solid which separates. In alloys of this type there is *no eutectic point*; the freezing point alters continuously with the composition throughout (Diagram IV). In alloys of the first two
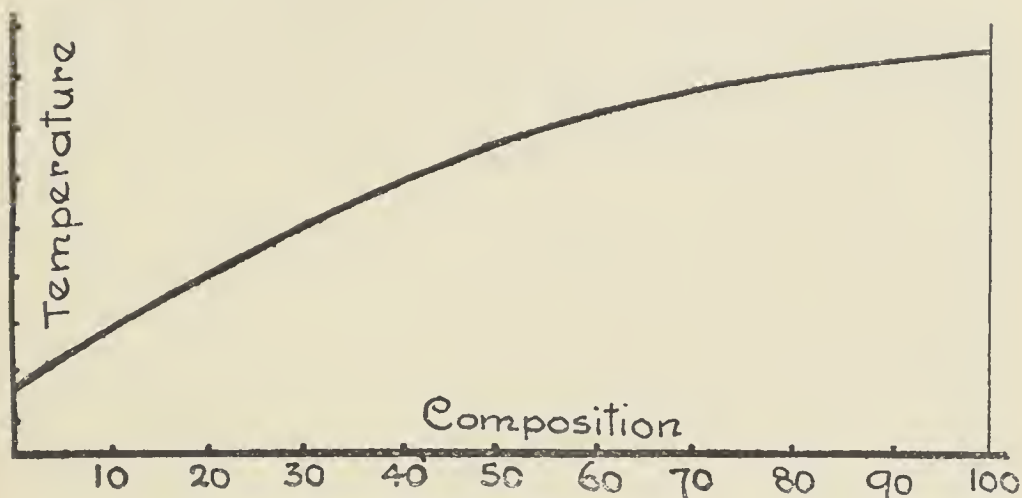

Diagram IV.

types, the freezing point and the melting point of an alloy of a given composition are the same; in solid solutions however this is not the case. [The temperature at which solid just begins to appear on cooling the fused mass is called the freezing point and the temperature at which liquid just begins to appear on heating is called the melting point. The curves representing the change of freezing point and melting point as the composition alters are called the "liquidus" and "solidus" curves respectively.]

(c) *The rate of cooling.* If the fused alloy is allowed to cool gradually and the temperatures are noted at definite times, it will be found that the fall of temperature continues regularly until solidification begins. In case of a pure metal, or a pure chemical compound, the temperature will then remain stationary as long as solid continues to separate; when all is solidified the temperature will again fall regularly as time goes on. If we map out the results by taking temperatures as ordinates and times as abscissae (see page 36), we shall observe an "arrest point" at the time when solid first begins to separate and this will be followed by a horizontal line representing the co-existence of solid and liquid; when all is solidified, the line again slopes downwards (a) Diagram V.

In case of an alloy of the eutectiferous type, we shall also get an arrest point when the solid first begins to appear; but now, instead of a horizontal line, we shall obtain a sloping line; this is

because the composition of the solution is continually altering as solid separates. The curve continues to slope downwards as long as one metal only solidifies; when however the composition of the liquid corresponds to the eutectic composition, the second metal begins to separate as well and now, at the eutectic point, we again get an arrest point in the curve followed now by a horizontal line representing the co-existence of the *two* metals and liquid (*b*).

In the case of alloys of the third type we obtain arrest points when the solid first begins to separate and when the whole solidifies; but the curve at these points shows only slight change of direction and there are no horizontal lines (*c*).
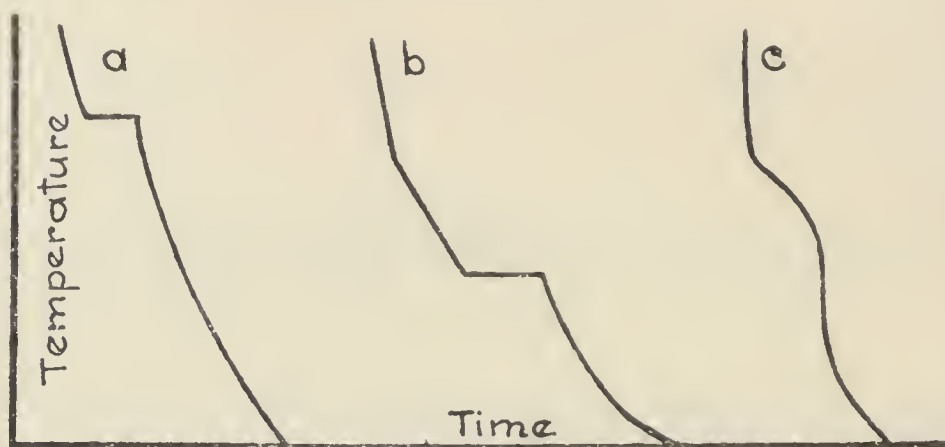

Diagram V.

33. The Phase Rule. The consideration of the conditions of equilibrium in *heterogeneous* systems (see page 4) is often considerably simplified by the application of a general law known as the Phase Rule. This rule has been deduced from theoretical reasoning which cannot be discussed here; it will be sufficient for our purpose to state the rule and to give some typical examples of its application.

Many instances have been already given of heterogeneous systems which are in equilibrium under certain stated conditions. Thus we saw that water can be in equilibrium with its vapour at various temperatures, but only if, for each temperature, the vapour pressure has a definite fixed value. At 100°, for example, the pressure of the vapour is 760 mm. If the pressure is greater or less than this, the system will not be in equilibrium;

vapour will condense, or water will vaporise, until the vapour has the required pressure. Water can also be in equilibrium with ice and water vapour, but in this case there is only one temperature and one vapour pressure at which the equilibrium can exist, namely, $0.0076°$ and 4.6 mm. Such a system is said to have no *degree of freedom* or to be a *non-variant* system. The system water—water vapour, on the other hand, has one degree of freedom or is *univariant*; we can have any temperature, within certain limits, provided we suitably adjust the pressure, or any pressure within certain limits provided we suitably adjust the temperature.

Solid salt, again, can be in equilibrium with its saturated solution and water vapour at various temperatures; but at any one temperature there will always be a definite, fixed, concentration of the solution and a definite vapour pressure. This system then has one degree of freedom. If however solid ice is also present, the system can only be in equilibrium at one definite temperature, at which the vapour pressure and the concentration of the solution also have definite and fixed values; the system now is invariant, i.e., it has no degree of freedom. An unsaturated solution of salt, the solid being absent, has two degrees of freedom; we can have various concentrations and vapour pressures at a given temperature without destroying the equilibrium. But if we fix the temperature *and* the concentration of the solution, the vapour pressure will assume a corresponding fixed value.

If solid potassium chloride and magnesium chloride are in contact with their aqueous solution, the solution will, when equilibrium is attained, have a fixed concentration for a given temperature and the vapour pressure will also have a fixed value, i.e., the system has one degree of freedom. If however only one of the solid salts is present, the system has two degrees of freedom; we can then have various concentrations and vapour pressures for a given temperature. Note therefore

that to give a univariant system in the case of water and *one* salt, the presence of *one* solid phase, solution and vapour, suffices; whereas with *two* salts (having a common acid radicle) *two* solid phases are required.

In the above examples, we have considered systems made up of various components. Water, ice and water vapour is evidently a one component system; salt and water two components; two different salts (with a common acid radicle) and water, three components.

Now the phase rule tells us that there is a definite relation between the number of components (C), the number of phases (P) and the degrees of freedom (F).

In the examples mentioned these numbers are as follows:

	C	P	F
Water, ice, vapour	1	3	0
Water, vapour	1	2	1
Salt, saturated solution, ice, vapour	2	4	0
Salt, saturated solution, vapour	2	3	1
Unsaturated solution, vapour	2	2	2
$MgCl_2$, KCl, saturated solution, ice, vapour	3	5	0
$MgCl_2$, KCl, saturated solution, vapour...	3	4	1
KCl, solution of the two salts, vapour	3	3	2

Further examples are:

	C	P	F
Chalk, lime, carbon dioxide	2	3	1
Iron, oxide of iron, steam, hydrogen	3	3	2

The relation is always

$$P + F = C + 2,$$

which holds for all cases of equilibrium in heterogeneous systems whether the changes are "chemical" or "physical." This is the Phase Rule. Some further examples of its application will be found in following sections. There is some difficulty in defining the number of components of a system and the definitions need not be considered here. For the present purpose we can take the number of

components as the *least* number of constituents from which we can produce all the phases. Thus, we could produce all the phases in the system chalk, lime, carbon dioxide, from calcium, carbon and oxygen. But we can also produce them simply from lime and carbon dioxide. We therefore say that the system has two components and not three.

Osmotic Pressure.

34. Many cases are known of substances which will allow the free passage through them of one constituent of a mixture and will not allow the passage of the other constituent. Thus if a mixture of hydrogen and nitrogen is contained in a heated palladium vessel, it is found that the hydrogen passes through the walls of the vessel but the nitrogen does not. If a mixture of albumen and common salt in aqueous solution is placed in a vessel closed by a bladder and the bladder is immersed in water, the salt passes through the bladder, but the albumen does not pass, or passes only to a very slight extent. Similarly, it is found that water can pass easily through copper ferrocyanide whereas most substances dissolved in water are unable to pass. This property is called *semi-permeability*; a plate or layer of copper ferrocyanide, for example, is termed a semi-permeable membrane, or semi-permeable partition, as regards water and substances dissolved in water.

If a vessel of porous clay, in the walls of which a membrane of copper ferrocyanide has been formed, is nearly filled with a solution of salt or sugar and immersed in water, it will be found that the water passes into the vessel and the level of the liquid becomes higher inside the vessel than outside. This will continue until a certain level is reached when equilibrium will result, i.e., water no longer enters from outside. This maximum level will depend upon the strength of the solution and the temperature. It is evident that the pressure of the liquid on the walls of the vessel must now be greater inside than it

is outside. The simplest way of measuring this pressure is to connect the top of the vessel with a mercury manometer and, instead of allowing the water to flow in from outside, to pour mercury into the manometer until its pressure is just sufficient to prevent any water from entering. In this way the volume of the solution in the vessel remains constant and the final maximum pressure is measured by the height of the mercury column in the manometer. This phenomenon is a slow one and it may take weeks or months before the maximum pressure is reached. This maximum pressure is called the osmotic pressure of the solution.

Laws of osmotic pressure. Experiments have shown that:

(1) For a given dissolved substance, the osmotic pressure is directly proportional to the concentration of the solution. This at once reminds us of Boyle's law for gases: the volume of a gas is inversely as the pressure and the concentration is inversely as the volume; if the volume remains constant, the pressure varies directly as the concentration.

(2) The osmotic pressure varies directly as the absolute temperature, just as the pressure of a gas does (Charles' or Gay Lussac's law).

(3) At a given temperature, solutions of various substances of the same *molar* strength (i.e., which contain the same number of gram-molecules per litre) exert the same osmotic pressure. [Acids, salts and bases do not obey this law, but exert a pressure which is greater than the calculated value; this is completely explained by the theory of ionisation. See Chapter VII.]

(4) The actual pressure obtained, for a given weight of a substance contained in a given volume of solution, is approximately the same as the gaseous pressure would be if the substance were completely gasified at the same temperature and confined in the same volume.

These laws may be expressed by saying that the gaseous laws and Avogadro's hypothesis are applicable to

substances in solution, if for gaseous pressure we sub-
stitute osmotic pressure. In the relation $PV = RT$, the
constant R has the same value, for molecular quantities
of dissolved substances, as it has in the case of gases.
When this principle is used for determining molecular
weights, we proceed exactly as in calculating the molecular
weight from the vapour density. For example, a solution
containing one gram of cane sugar in 100 c.c. at 0° was
found to give an osmotic pressure of 490 mm. As in the
case of gaseous density, we first correct the volume for
temperature and pressure,

$$100 \times \frac{273}{273 + 0} \times \frac{490}{760} = 64 \cdot 47 \text{ at } 0° \text{ and } 760 \text{ mm.}$$

The molecular weight is the weight contained in 22,400 c.c.
at 0° and 760 mm. (see page 24) and is therefore

$$\frac{22400}{64 \cdot 47} = 347.$$

Allowing for probable error, this is practically the same
as the molecular weight (342) deduced from chemical
considerations.

No great exactness can be expected owing to the
difficult character of the experiment, but, as in the case
of vapour density, the object of the determination is, in
general, only to find the correct multiple of the simplest
formula, e.g., to ascertain whether the molecular formula
for cane sugar is $C_{12}H_{22}O_{11}$ or some multiple of this. In
practice the determination is usually carried out in-
directly, as will be described below.

It was previously mentioned that the determination
of molecular weights by the vapour density method
sometimes gives numbers which are much smaller
than those required from direct chemical reasoning
(e.g., NH_4Cl); in other cases the numbers found are too
large (e.g., acetic acid). These "abnormalities" were
explained by "dissociation" and "association" respec-
tively. Just the same apparent abnormalities may

appear when molecular weights are determined by osmotic pressure and they are explained in the same way.

A very dilute solution of potassium chloride, for example, has an osmotic pressure which would, by the above simple calculation, give a molecular weight of $\frac{39 + 35 \cdot 5}{2}$, i.e., the osmotic pressure is about twice as great as would be expected if the substance dissolved unchanged. But if we assume that the salt has split up into two parts and each part now behaves as an individual, the result is easily accounted for. The osmotic pressure depends on the molecular concentration, i.e., the number of molecules in a given volume; in the case mentioned each of the parts into which the salt has dissociated behaves, as regards osmotic pressure, as if it were a molecule.

35. Solutions which have the same osmotic pressure are called *isotonic*. Evidently therefore isotonic solutions have the same molecular concentration. In making this statement it is understood that the parts into which acids, salts and bases may split up in solution are, for this purpose, to be regarded as molecules.

As an example: the molecular weights of cane sugar, urea and potassium chloride are 342, 60 and 74·5, respectively, and very dilute solutions of these three substances are isotonic when, in equal volumes of the solutions, the quantities are in the ratio of 342 : 60 : 37·25.

Certain plant cells contain solutions of substances enclosed in a thin elastic envelope which has semipermeable properties—water can pass through the envelope but the substances in solution cannot. If such a cell is placed in pure water, it begins to swell; water tends to pass in since the molecular concentration is greater inside. If placed in a strong salt solution the envelope shrinks, since water passes out. When the solutions inside and outside are isotonic, it neither swells nor shrinks. On this principle de Vries succeeded in comparing the

molecular concentrations of certain dissolved substances. If we have solutions of two different substances, of known concentration, which are isotonic and we know the molecular weight of one substance, that of the other can be deduced (dissociation, etc., being excluded or allowed for).

36. The determination of molecular weights of dissolved substances. The method briefly described above of directly measuring the osmotic pressure is difficult to carry out owing to the long time required to reach the final pressure. This pressure, moreover, is very high, even for moderately strong solutions, and breakage of the membrane or the connections may take place unless special precautions are taken. The semi-permeable membranes, again, are, as a rule, far from perfect, although it is possible to construct them nearly so in certain cases.

It happens however that there are many properties of solutions which depend directly on osmotic pressure and are proportional to it. These properties can be easily and accurately measured and serve therefore for molecular weight determination. Two of these properties, which are largely made use of, will be shortly described here.

The lowering of the freezing point. It has long been known that an aqueous solution of a substance freezes at a lower temperature than pure water—sea water, for example, freezing below 0°. Further it has been shown that this lowering of the freezing point is directly proportional to the concentration of the solution (Blagden's law). Thus, if w grams of a substance when dissolved in a given quantity of water lower the freezing point by t degrees, one gram of it dissolved in the same quantity of water will lower the freezing point by $\dfrac{t}{w}$ degrees. Later experiments demonstrated that this lowering is the same for solutions of different substances of equal molecular concentration, provided that the

substances do not dissociate (ionise) when dissolved*. Raoult showed, in fact, that for such substances (i.e., for non-electrolytes) the following relation holds (Raoult's law):

$$\frac{t}{w} \times M = C,$$

where t is the lowering of the freezing point, w is the weight of substance dissolved in 100 grams of water, M is the molecular weight of the substance and C is a constant which depends on the nature of the solvent. The value of this constant was, in the first instance, found by trial with substances of known molecular weight. It may however be calculated from the latent heat of fusion of the solvent by means of thermodynamical reasoning: in this way it can be shown that $C = \dfrac{2T^2}{100L}$, where T is the freezing point of the solvent on the absolute scale and L is the latent heat of fusion. Thus C for water is $\dfrac{2 \times (273)^2}{100 \times 79}$ or about 18·8. For acetic acid C is about 39 and for benzene about 49.

The experiment is carried out as follows:

A weighed quantity of the solvent (usually 10 to 20 grams), placed in a suitable vessel, is cooled by a bath which is kept one or two degrees below the freezing point of the solvent. The liquid is allowed to fall to about half a degree below the freezing point (i.e., it is "supercooled") and is then vigorously stirred; this causes sudden freezing and the temperature is noted on a very delicate thermometer immersed in the liquid. The vessel is then taken out of the bath, the ice allowed to melt and a weighed quantity (0·1 to 0·2 gram) of the substance to be examined is introduced. When all is dissolved, the freezing point of the solution is determined as before. If S grams of solvent and w gram of solute

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* It follows that isotonic solutions of different substances in the same solvent have the same freezing point.

are taken and t is the observed lowering of the freezing point, the formula becomes

$$\frac{S}{100} \times \frac{t}{w} \times M = C \quad \text{or} \quad M = \frac{100Cw}{St}$$

[since C was determined for 100 grams of solvent and the lowering varies directly as the concentration].

37. *The lowering of the vapour pressure.* The vapour pressure of a liquid, at a given temperature, is lowered when a substance (non-volatile) is dissolved in it, and this lowering is proportional to the concentration. Raoult discovered, further, that solutions, in the same solvent, of equal molecular concentration, have the same vapour pressure, and he showed that, for solutions which are not too concentrated, the following relation holds:

$$\frac{P - P'}{P} = \frac{n}{N + n},$$

where P is the vapour pressure of the pure solvent, P' that of the solution and N and n are the number of gram molecules of solvent and of solute, respectively. $\left[\dfrac{P - P'}{P}\right.$ is called the relative lowering of the vapour pressure.$\left.\right]$ Note that "number of gram molecules" means the weight in grams taken divided by the molecular weight. Thus in the experiment we dissolve w gram of solute in S grams of solvent; M is the molecular weight of the solvent (as deduced from its vapour density) and x is the required molecular weight of the solute. The relation is then

$$\frac{P - P'}{P} = \frac{\dfrac{w}{x}}{\dfrac{S}{M} + \dfrac{w}{x}},$$

or

$$x = \frac{wMP'}{S(P - P')}.$$

The actual direct determination of the lowering of the vapour pressure is difficult and the results are not usually very accurate owing to the small difference between P and P'. It is much more convenient in practice to determine instead the *rise in the boiling point*. A liquid boils when its vapour pressure is equal to the pressure of the atmosphere above it; hence if the pure liquid boils at $t°$ it is evident that, when a solute is dissolved in it, it will have to be heated *above* $t°$ to make it boil. For small elevations of the boiling point the elevation is, sufficiently nearly, proportional to the concentration of the solution, so that the results may be calculated as in the freezing point experiment. It is usual to calculate the boiling point constant, C, for one gram or for one c.c. of solvent instead of for 100 grams as in the freezing point constant. The formula is therefore

$$M = \frac{Cw}{st},$$

where s is the weight (or volume) of solvent, w the weight of solute and t is the rise of boiling point.

There are many other ways in which the lowering of the vapour pressure may be determined.

38. It may appear difficult at first to understand in what way the lowering of the freezing point, or of the vapour pressure, is connected with the osmotic pressure of the solution. Whatever the nature of osmotic pressure may be, it is evident that its effect is to make the solution apparently strive to become weaker. In the experiment previously referred to (page 69) water passes into the solution through the semi-permeable partition and dilutes the solution; this continues indefinitely if the pressure inside is not allowed to rise. Similarly, if an aqueous solution is contained in an open vessel and placed next to an open vessel of water (the whole being under a bell jar, preferably with the air removed), it will be found that water vapour distils from the water into the solution, the latter becoming more dilute. [Or if the two vessels

contain a strong and a weak solution, vapour will distil from the weaker to the stronger until the solutions are isotonic.] This phenomenon is quite analogous to the unlimited expansion of gases (page 11): a given quantity of any gas always tends to fill any vessel however large.

Now when a solution freezes, the solid which at first separates is the *pure solvent**; it follows therefore that the solution remaining must get stronger as the solid separates. Similarly, when a solution of a non-volatile solute vaporises, the vapour is that of the pure solvent and the solution must become stronger as vaporisation proceeds. Work has therefore to be done against the osmotic pressure, just as work has to be done if the volume of a gas is diminished. [We can calculate this *osmotic work* exactly as we calculated the work done by a gas in expanding. See Section 12.] It can be shown by thermodynamics that the temperature at which the solid is in equilibrium with the liquid must be lower for the solution than it is for the pure solvent; similarly, that the pressure of the vapour at a given temperature must be lower for the solution than for the pure solvent. This is analogous to the lowering of the melting point of ice by increased pressure; water occupies a larger volume in the solid than in the liquid state and, when the solid is formed, work has to be done against the superincumbent pressure.

39. We will attempt here to give a brief elementary sketch of the way in which we can apply this knowledge to calculate Raoult's freezing point constant from the latent heat of fusion of the solvent.

If we cool a dilute aqueous solution of a substance to its freezing point and allow some of the pure solvent to separate as ice, we can separate this ice, warm the whole system up to 0° and allow the ice to melt again at this temperature. The result is that we have a

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* There are exceptions to this; when the solute and solvent can form a solid solution, both may separate together. See page 57. To such cases the freezing point method is not applicable.

solution which is stronger than the original solution and, separated from it, we have the liquid water resulting from the melted ice. We now place the solution in a cylinder which has a semi-permeable bottom, and is fitted with a piston, and allow the liquid water to enter the cylinder through the semi-permeable partition. The solution in the cylinder will become diluted and the piston will rise; as it rises work is done against the superincumbent pressure. If we now cool the whole system to the freezing point of the solution, everything is in the same condition as it was at the beginning. All that has happened is that heat has been absorbed at the higher temperature and evolved at the lower temperature and that a certain amount of work has been done. We may then regard this as a *heat engine* or a machine for converting heat into work; having restored everything to the original condition we can repeat the processes as often as we like. [Also, we might work the machine *backwards*, by first placing the original solution in the cylinder and, by applying pressure on the piston, force out a certain quantity of the pure solvent; this is then frozen at $0°$, the whole system cooled to the freezing point of the solution and the ice is then mixed with the solution and allowed to melt at the *lower* temperature.]

If these operations are carried out under the most favourable conditions, it can be shown that the heat absorbed at the higher temperature is to the work done, as the higher temperature (on the absolute scale) T_1 is to the difference of temperature $T_1 - T_2$.

Note particularly that the heat engine can only convert heat into work if there is a *difference* of temperature. Heat is taken in at the higher temperature and given out at the lower temperature; but the heat given out is less than that taken in by the heat-equivalent of the work done. In an ideal engine working under the most favourable conditions, the maximum quantity of work obtainable is $\dfrac{T_1 - T_2}{T_1}$ of the heat taken in.

Suppose now we have a dilute solution containing n mols of solute dissolved in 100 grams of solvent. Let the freezing point of the solvent be T and that of the solution $T - t$ (i.e., let the lowering of the freezing point be t). Let us go through the operations outlined above, freezing out, at $T - t$, just $\dfrac{100}{n}$ grams of solvent; this is the quantity of solvent which contained one mol of solute*. We now separate the solid, warm the whole system to T and allow the

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* The quantity of solution is supposed to be large, so that this operation does not materially alter the concentration. It is also assumed that the solution is so dilute, and t so small, that the heat required to warm the system through this range is negligible in comparison with the latent heat of fusion of ice.

solid to melt; the heat absorbed in melting it will be $\dfrac{100L}{n}$, where L is the latent heat of fusion. The resulting liquid solvent is allowed to enter the cylinder through the semi-permeable diaphragm while a constant pressure P, equal to the osmotic pressure of the solution, is kept on the piston. If V is the resulting increase of volume of the solution, the work done is PV. But V is the volume which contained 1 mol; hence $PV = 2T$, since the gaseous laws apply to solutions. [That is to say, the work done is the same as that which would be required to produce one mol of a gas at T.] From the relation given above

$$\frac{\left(\dfrac{100L}{n}\right)}{PV} = \frac{T}{t}, \quad \text{or} \quad \frac{t}{n} = \frac{2T^2}{100L}$$

But by Raoult's formula, $t = Cn$. Hence

$$C = \frac{2T^2}{100L}.$$

40. There are several other methods of determining the molecular weight of substances in solution, all depending more or less directly on osmotic pressure. Brief mention may be made, for instance, of the "lowering of solubility" method (Nernst). A solute placed in a solvent may be supposed to have a solution pressure, analogous to a vapour pressure, which represents its tendency to throw off its molecules into the solution, just as a liquid tends to give off its molecules into the space above it. If now a substance is dissolved in the solute—which may be either a liquid or solid—the solution pressure is lowered. The solution becomes saturated when the solution pressure of the solute is equal to the osmotic pressure of the solution. Hence by determining the concentration of the solution, i.e., determining the solubility, at a given temperature, first of the pure solute and then of the solute with a weighed quantity of the substance dissolved in a given quantity of it, we can calculate the molecular weight of the substance, using a similar formula to that given for the lowering of the vapour-pressure.

41. It must be distinctly understood that the determination of the molecular weight of a substance in

solution gives us no information as to the molecular weight of the *pure* substance in the liquid or solid state. Of the molecular weights of pure liquids or solids we know very little. There are however ways in which we can compare the molecular weights of liquids to the extent that, if one is assumed to exist as single molecules, we can tell with a certain degree of probability whether the other exists as single or as *associated* molecules.

41 a. Certain physical properties of liquids show a regularity in their relationships or in their behaviour under varying conditions. Thus, for example, it is found that, in many cases, the ratio of the molecular latent heat of vaporisation to the boiling point (on the absolute scale) is constant (Trouton's rule). Also, that the rate of change of molecular surface energy with temperature is constant (Eötvös)*. Further, the boiling points of liquids often show more or less regular changes with composition. Thus C_2H_4 boils at $- 105°$, C_4H_8 at $- 5°$, C_8H_{16} at $126°$ and $C_{16}H_{32}$ at $274°$. Again, HCl boils at $- 100°$, HBr at $- 73°$ and HI at $- 25°$. One would therefore expect hydrofluoric acid to boil at a temperature considerably below $- 100°$, instead of which it boils at $+ 19°$. Now hydrofluoric acid in the state of vapour has been shown to have the simple molecular formula above $100°$, but as the temperature falls it becomes more complex, corresponding to about H_2F_2 at $50°$ (at ordinary pressure). Consequently it appears probable that the reason of its abnormally high boiling point is to be found in its *associated* condition. Again, hydrogen sulphide boils at about $- 62°$ and water would be expected to boil at a still lower temperature†, whereas it boils at $+ 100°$. In this case we cannot show any association in the vapour state, but the abnormally high boiling point may well be explained by supposing that the molecules are associated in the liquid state. Now water and certain other liquids, such as fatty acids and alcohols,

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* If D is the density of a liquid and M its molecular weight, $\dfrac{M}{D}$ is called the molecular volume (see Section 51). If we take the values of the molecular volumes of various liquids and bring these values to the $\frac{2}{3}$ power, we obtain numbers proportional to their "molecular surfaces," i.e., surfaces in which there is an equal number of molecules. Calling the molecular volume MV the molecular surface is proportional to $(MV)^{\frac{2}{3}}$, and this value multiplied by the surface tension of the liquid is called the molecular surface energy.

† Since oxygen compounds usually boil at much lower temperatures than corresponding sulphur compounds, compare CO_2 and CS_2, or $(C_2H_5)_2O$ and $(C_2H_5)_2S$.

all show marked deviations from the regularities in the relationships of their physical properties referred to above. Hence it is usual to regard these liquids as "associated," i.e. as consisting, to a large extent, of molecules greater than those represented by the simple chemical formulae derived from vapour density determination. Examples of non-associated liquids, which show a normal behaviour, are benzene, chlorobenzene, carbon tetrachloride, carbon disulphide, ether, aniline. As "associated" liquids, may be mentioned water, alcohols, fatty acids, acetone, propionitrile, nitroethane.

It is a remarkable fact that if we determine molecular weights of dissolved substances by osmotic methods (e.g., freezing point depression), using any of these associated liquids as solvent, we usually obtain the simplest formula; whereas many substances dissolved in the non-associated solvents give molecular weights which are abnormally high. E.g. benzoic acid in water gives $C_6H_5 . COOH$ and in benzene $(C_6H_5 . COOH)_2$. The molecular weights of electrolytes, moreover, come out too low when water is used as solvent, whereas in non-associated solvents (when they happen to be soluble) they give normal results. Thus, the solvents which are themselves associated tend to prevent the association of substances dissolved in them and, in the case of electrolytes, even to cause them to break up into still simpler units. In consequence of their behaviour towards electrolytes, these associated solvents are often spoken of as *ionising* solvents (see Chapter VII) since the two properties seem to be closely related. There appears also to be a close relation between the ionising property of these liquids and their behaviour as dielectrics, i.e., the solvent of greater ionising power has, as a rule, the higher dielectric constant* (Nernst-Thomson rule).

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* The attraction between two oppositely electrified bodies having charges ϵ_1 and ϵ_2, which are at a distance d apart, may be expressed as $\frac{\epsilon_1 \epsilon_2}{Kd^2}$, where K is a constant depending on the nature of the medium and is called the *dielectric constant*.
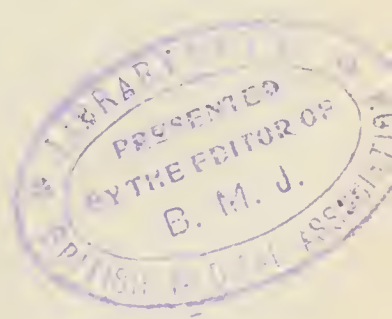
CHAPTER IV

ATOMIC WEIGHTS

42. The hypothesis that matter is made up of small individual parts dates back to the time of the ancient Greek philosophers; it was put into a definite and quantitative form by Dalton in 1803.

According to Dalton's "atomic theory" the small indivisible parts, or atoms, of a given element are all alike and have the same mass. The absolute mass of the atom has been calculated in various ways, but in general chemistry we are mainly concerned with the *relative* masses of atoms of different elements. If we choose to fix the atomic mass of hydrogen as unity, we say that the atomic mass of oxygen is 15·88, meaning that the mass of the atom of oxygen is 15·88 times that of the atom of hydrogen.

It has been mentioned that to each element we may assign a constant number representing its combining ratio, and it is evident that these constant numbers must be closely related to the atomic weights. If we define the equivalent weight as stated in Section 1, we may state this relation in the form

$$\text{equivalent weight} \times n = \text{atomic weight},$$

when n is a whole number, not exceeding 8.

Note that this implies that the equivalent weight has been determined by analysis or synthesis of the normal and stable compounds of the element of the simplest type; otherwise n might not be a whole number. In other words, if we wish to make use of the relation in determining atomic weight, we should not deduce the equivalent weight of the element from such compounds as N_3H or from complex hydrocarbons.

Since the same element may have more than one equivalent weight, it is evident that this small whole number will vary according to which equivalent weight

is chosen. Thus the equivalent weight of tin in the stannous compounds is 59·5 and in the stannic compounds 29·75. The atomic weight of tin is proved to be 119 so that n is either 2 or 4. In determining atomic weights it must be clearly understood that the first essential step (when possible) is to determine the *equivalent* weight with the greatest accuracy. Having done this, we must seek for some independent method of ascertaining what is the small whole number by which we are to multiply the equivalent weight in order to find the atomic weight. [In the case of elements like helium and argon which refuse to combine with anything, we cannot, of course, determine the equivalent weights. Indirect methods must then be applied. See below.]

43. Methods of fixing the atomic weights of the elements.

(1) *Determination of the weight of the element contained in one molecular weight of its compounds.* Since one molecule of the element itself, or of any of its compounds, must contain at least one atom of the element, it is evident that if we determine the molecular weights of various compounds of the element and then ascertain in each case what weight of the element is contained in this molecular weight, the smallest number so obtained will, in all probability, be the atomic weight; the atomic weight cannot at any rate be greater than this. It is true, it may be less; but if we take a sufficiently large number of compounds, it is probable that some of them, at any rate, will only contain a single atom of the element. Hence the usual statement that *the atomic weight of an element is the least weight of it which is ever found in one molecule of any of its compounds.*

If, for example, the atomic weight of carbon is required, we may determine the molecular weights of various carbon compounds and then, by analysis, estimate how much carbon is contained in one molecular weight of each. This has been done with many thousands of

carbon compounds and the smallest weight ever found is 12. Hence we conclude that this is the atomic weight of carbon. [If someone were to discover a new carbon compound in one molecular weight of which there were only 6 parts of carbon, we should, of course, have to adopt this number instead. Or again, if a carbon compound were found to contain 18 parts of carbon in one molecular weight, we should have to abandon the atomic weight 12, because one molecule must contain a whole number of atoms; we should then have to conclude that the maximum atomic weight was 6.]

44. (2) *The specific heat rule of Dulong and Petit.* If we have accurately determined the equivalent weight of an element we may safely conclude that the atomic weight is either identical with or is a simple multiple of this number, as indicated (Section 42) by the relation

atomic weight = equivalent weight × *n*.

Since the equivalent weight is, in most cases, a relatively large number, it is evident that if we can by any means find the *approximate* value of *n* it will be sufficient for our purpose.

Now Dulong and Petit in 1818 observed that many of the atomic weights which were accepted at that time varied inversely as the specific heats* of the elements in the solid state: that is to say,

atomic weight × specific heat = a constant.

The value of this constant was somewhere about 6·4.

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* The specific heat of a substance may be defined as the thermal capacity of unit mass of it, i.e., as the quantity of heat required to raise the temperature of unit mass of the substance through one degree. If Q units of heat are required to raise the temperature of w grams of the substance through t degrees, the specific heat is $S = \dfrac{Q}{wt}$, assuming that the value does not change with temperature. As a matter of fact it does change, more or less, in nearly all cases and, if we wish to be quite accurate, we should speak of the specific heat *at* a particular temperature, defining its value in terms of infinitely small quantities, dQ and dt. The value will then be $S = \dfrac{1}{w} \cdot \dfrac{dQ}{dt}$.

In other cases however it was necessary to multiply the accepted values by a whole number in order to make the rule applicable.

Assuming the truth of this relation, we may choose as our atomic weight that multiple of the equivalent weight which brings it into harmony with the rule, i.e.,

$n \times$ equivalent weight $\times$ specific heat $= about$ 6·4.

As examples of the application of this rule: the specific heats of silver, zinc and aluminium are, approximately, 0·056, 0·093 and 0·225, and the equivalent weights, respectively, are 108, 32·68 and 9. If the above constant is taken as 6·4 we shall have for the value of n,

for silver, $$n = \frac{6·4}{108 \times ·056} = 1·06,$$

for zinc, $$n = \frac{6·4}{32·68 \times ·093} = 2·1,$$

and for aluminium, $$n = \frac{6·4}{9 \times ·225} = 3·11.$$

But, according to theory, n must be a whole number, the difference obtained being due to the uncertain value of the constant and to experimental error in the determination of specific heats. We therefore take as the atomic weights

Ag $= 108$, Zn $= 32·68 \times 2$, and Al $= 9 \times 3$.

Note particularly that it would be quite useless to attempt to determine the exact atomic weight of an element, from the specific heat alone, by application of Dulong and Petit's rule. *It is necessary first to know the equivalent weight exactly*: the specific heat rule then guides us as to which multiple of the equivalent weight is to be taken as the atomic weight.

44 a. There are many elements which do not conform to this rule. Thus the product of specific heat and atomic weight in the case of the following elements is found to be

C, 1·8,   H, 2·3,   B, 3·7,   Si, 3·8,   O, 4,   P, 5·4,   S, 5·4.

It may be observed however that the specific heats of carbon, boron and silicon increase rapidly with rise of temperature up to a certain point and at about this point the product of atomic weight and specific heat approximates to the common constant. At very low temperatures all the elements give low values and there is considerable divergence in the values for different elements. The following numbers have been obtained for the product at a temperature of about 25 to 35 degrees above absolute zero:

Cu, 0·223, Ag, 1·58, Pb, 2·96, Al, 0·25, C, 0·0.

On the whole, it is questionable whether we have any right to select the value at the temperature which best fits in with our theories; the fact remains however that the values between 0° and 100° do often agree well with other methods.

The product specific heat × atomic weight is called the *atomic* heat. If the above rule were true in all cases we might express it by saying that, in the solid state, "all atoms have the same capacity for heat"; i.e., that the same quantity of heat is required to raise the temperature of one gram atomic weight of any element through 1°.

Neumann's extension of Dulong and Petit's rule. In many cases it appears that the atomic heat is an "additive" property, that is, that the molecular heat is equal to the sum of the atomic heats of the elements contained in the molecule. Thus the molecular weight of potassium chloride is 74·5 and its specific heat is 0·173; the product 12·44 is about twice the common constant. The product of molecular weight and specific heat of mercuric iodide is 19·07, or about three times the common constant. This rule seems to hold even if the atomic heats are "abnormal." Thus, the specific heat of ice is 0·474 and the molecular weight 18; the product is 8·5, whereas the sum of the separate atomic heats is $2 \times 2·3 + 4 = 8·6$.

It might at first sight appear that this extension of the rule could be used to find molecular weights, but, of course, this is not so. We should have two unknown quantities, the molecular weight and the number of atoms in the molecule; if we double one we double the other, and so on.

45. (3) *The law of isomorphism.* It often happens that different substances crystallise in the same form and are capable of forming mixed crystals (isomorphous mixtures); generally, a crystal of one can go on growing in a solution of the other, the relative proportions of the two substances in a single crystal being continuously variable. Thus, common alum, $KAl(SO_4)_2 . 12H_2O$, can crystallise in all proportions with chrome alum, $KCr(SO_4)_2 . 12H_2O$, or with ammonium alum $(NH_4)Al(SO_4)_2 . 12H_2O$.

In such cases there is always a similarity of chemical formula between the two substances, and this fact may serve to guide us in fixing the atomic weight of an element. When gallium was first discovered, for example, the equivalent weight was found to be 23·3, but there was no evidence to show whether the atomic weight was 23·3, 46·6, 69·9 or some higher multiple. But gallium sulphate and ammonium sulphate were found to crystallise together forming an alum isomorphous with ammonium alum. The difference in composition in these two alums is that 69·9 parts of gallium in the one are replaced by 27 parts of aluminium in the other, and, since the chemical formulae of the two must be analogous, it is evident that 69·9 must be taken as the atomic weight of gallium if 27 is the atomic weight of aluminium.

(4) *Application of the periodic classification.* This method has been instrumental in deciding many doubtful cases, notably those of beryllium, indium and uranium. Further reference to this will be made on page 110.

46. (5) *Determination of the gaseous density and atomicity of the element itself.* Since (in the units adopted on page 22) molecular weight = gaseous density × 2, it is evident that the atomic weight of an element

$$= \frac{2 \times \text{gaseous density}}{\text{numbers of atoms in the molecule}}.$$

The number of atoms in a molecule is called *atomicity*

so that $$\text{atomic weight} = \frac{\text{density} \times 2}{\text{atomicity}}.$$

Hence if we can determine the atomicity by some independent method, we can calculate the atomic weight of an element from its density in the gaseous state. [Note particularly that we cannot find the atomic weight from the density *alone*; this would only serve to give us a *maximum* value.]

Owing to the difficulty of sufficient exactness in gaseous density determination and to the deviations from the gas laws (page 16), this method was, until a comparatively recent date, only used to obtain an approximation, the exact value being deduced from the equivalent weight. But with improved experimental methods and the application of van der Waals' theory, exact results may be obtained.

In the cases of helium, argon, neon, krypton and xenon, this is practically the only method available for finding the atomic weights, since these elements form no compounds and, consequently, have no equivalent weights.

To find the atomicity. If we already know the atomic weight and density of an element its atomicity is given by the above relation. If we do not know the atomic weight, we have to seek some independent method. Such a method is afforded by the following considerations:

If the molecules of a gas consist of single atoms, i.e., if the gas is monatomic, it may be supposed that, when heat is applied to it, the heat used goes to increase the kinetic energy of the molecules, provided that the volume is kept constant. If, on the other hand, the molecules contain more than one atom, it is probable that, when heat is applied, some of the heat is used up in doing internal work in the molecules themselves (e.g., in increasing rotatory movement or in changing the relative positions of the atoms). If now we take one gram molecular weight of a monatomic gas at 0° and raise its

temperature to 1°, keeping the *volume constant*, we can calculate, from the kinetic theory, that 3 calories will be required.

[The kinetic energy of the molecules will be increased by $\frac{1}{273}$ of its value, so that the increase will be $\frac{1}{273}$ of $\frac{MU^2}{2}$. But $\frac{MU^2}{2} = PV \times \frac{3}{2}$ and $\frac{PV}{273} = 2$ in thermal measure (see page 13). Therefore

$$\tfrac{1}{273} \text{ of } \frac{MU^2}{2} = \tfrac{1}{273} \text{ of } PV \times \tfrac{3}{2} = 2 \times \tfrac{3}{2} = 3.]$$

If we perform the same operation with a polyatomic gas, i.e., with one whose molecules contain more than one atom, we shall require more than 3 calories in order to raise its temperature from 0° to 1°. Let us call this extra quantity of heat x. Then for the monatomic gas we require 3 calories and for the polyatomic gas $3 + x$ calories. It is probable, from our supposition, that x will be greater the more atoms there are in the molecule.

We might find this quantity of heat directly by heating the gas to a given temperature in a closed vessel, plunging it into a known quantity of water and observing the rise of temperature in the latter. But in practice it is easier to make the experiment at *constant pressure*, so that the gas is allowed to expand on heating. But here, external work is done in overcoming the atmospheric pressure so that more heat will be required. For one gram molecule of a gas, when heated from 0° to 1°, this external work will be, in thermal measure, 2 calories (see above). We may express this by saying that the molecular specific heat of a gas at constant pressure (C_p) exceeds that at constant volume (C_v) by 2 units. If therefore we experimentally determine the molecular specific heat at constant pressure we have merely to subtract 2 units in order to obtain the value at constant volume.

For a *monatomic* gas the values will therefore be $C_v = 3$ and $C_p = 5$, and the ratio $\dfrac{C_p}{C_v}$ will be $\frac{5}{3} = 1\cdot67$.

For *polyatomic* gases the value x has to be added to each, so that $\dfrac{C_p}{C_v} = \dfrac{5 + x}{3 + x}$. This ratio must be less than $1\cdot67$ and will be smaller as x is larger, i.e., the more atoms there are in the molecule the smaller will be the value of $\dfrac{C_p}{C_v}$.

Now C_p for hydrogen, nitrogen, hydrogen chloride and carbon monoxide is found to be about $6\cdot8$. C_v is therefore about $4\cdot8$ and the ratio $\dfrac{C_p}{C_v}$ is $\dfrac{6\cdot8}{4\cdot8} = 1\cdot41$. For hydrogen sulphide the ratio is $1\cdot31$ and for marsh gas $1\cdot27$. These results therefore agree well with the theory since the more atoms there are in the molecule the smaller is the ratio. [There are, however, some abnormal cases.] Instead of actually measuring the specific heats, we can find the ratio $\dfrac{C_p}{C_v}$ by an indirect method, namely, by comparing the velocity of sound in the gas with that in some gas for which the value of the ratio is known*.

Now by this method it has been shown that the value of the ratio in mercury vapour is $1\cdot67$. Since we know from the atomic weight and vapour density of mercury vapour that the molecular weight is the same as the atomic weight, i.e., that mercury vapour is monatomic, this result is strikingly in agreement with theory.

The value of the ratio in helium, neon, argon, krypton and xenon is also found to be $1\cdot67$. Therefore it is concluded that these gases are monatomic. In order to find their atomic weights therefore, we have merely to multiply their densities by 2.

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* By means of the formula $V = \sqrt{\dfrac{P}{D} \cdot \dfrac{C_p}{C_r}}$, where V is the velocity, P the pressure and D the density.

In addition to the foregoing methods of fixing the values of the atomic weights, information may in some cases be obtained from relationships between the atomic weights and the wave lengths of certain characteristic lines in the spectra of allied elements. Further, it has recently been shown that there is a relation between the atomic weights of the elements and their transparency to Röntgen rays (see Section 103).

47. Relation between atomic weight and equivalent weight. It has been stated above that this relation is a simple one, namely, that

$$E \times n = A,$$

where E is the equivalent weight, A the atomic weight and n is a small whole number. This whole number (which is never greater than 8) expresses then the ratio $\dfrac{A}{E}$ or the number of times that the atomic weight contains the equivalent weight. Provisionally we will call n the *valence* or *valency* (1st definition). Its value will, of course, depend upon the source from which the equivalent weight has been deduced. Thus, if we determine the equivalent weight of mercury by analysing mercuric chloride, we obtain $E = 100$, whereas, by analysing mercurous chloride, the value obtained is 200. Since the atomic weight of mercury is 200, $n = 2$ in the first case and 1 in the second. We express this by saying that mercury is bivalent (or divalent) in the mercuric salts and univalent (or monovalent) in the mercurous salts.

This definition of valency is a simple and useful one (more especially for inorganic compounds) and the value can be obtained directly from practical measurements without making any assumptions. But it has generally been the custom to define valency in a somewhat different way, namely, as "atom linking capability," i.e., the valency of an atom in a given compound is the number

of other atoms with which it is in direct union. Since hydrogen, fluorine, chlorine, bromine, iodine, and the organic radicles methyl and ethyl are found to produce, as a rule, only *diatomic* molecules, whether in the free state or when combined together, these are regarded as *univalent* atoms or radicles, and we can, in the simpler cases, define the valency of a given atom as *the number of atoms of any univalent atom or radicle with which it directly combines* (2nd definition). It is evident that this number is, in the simpler cases, identical with that obtained by the first definition, namely, $\dfrac{A}{E}$; since the equivalent weight and the atomic weight of a univalent atom must, by either definition, be the same.

47 a. But a difficulty arises if we wish to define the valency of an element in those compounds which contain more than one atom of it in the molecule. Thus, in methane, CH_4, the valency of carbon is 4 by either definition; the equivalent weight of carbon is here $\frac{12}{4} = 3$ and $\dfrac{A}{E}$ is therefore 4. By the second definition, one atom of carbon unites with 4 atoms of a univalent element and is therefore 4. But in ethane, C_2H_6, the equivalent weight of carbon (as usually defined) is $\frac{12}{3} = 4$ and $\dfrac{A}{E}$ is $\frac{12}{4} = 3$. One atom of carbon unites with three atoms of hydrogen and the valency would therefore, at first sight, appear also to be 3. But in ethane we assume that the two atoms of carbon are directly combined together and we say therefore that carbon is here quadrivalent because one atom of it combines directly with four other atoms:

$$
\begin{array}{ccc}
\text{H} & & \text{H} \\
| & & | \\
\text{H---C} & \!\!\!\text{---}\!\!\! & \text{C---H} \\
| & & | \\
\text{H} & & \text{H}
\end{array}
$$
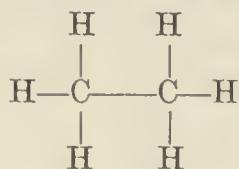
In other words, when more than one atom of the given element is present in a molecule, we can no longer define its valency by the second definition unless we make assumptions as to how the atoms are linked together. In ethylene, C_2H_4, we say that carbon is still quadrivalent because we assume that the two carbon atoms are united together by two valencies, and in acetylene, C_2H_2, we assume that they are linked by three valencies:

$$
\begin{array}{cc}
H & H \\
| & | \\
C\!\!=\!\!=\!\!C \\
| & | \\
H & H
\end{array}
\quad \text{and} \quad H\!-\!C\!\equiv\!C\!-\!H
$$
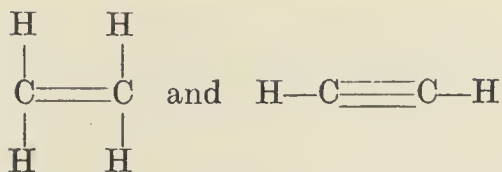
Evidently therefore the two definitions do not give the same result when more than one atom of the given element is present in the molecule. This discrepancy has, in the past, led to a good deal of misunderstanding, notably in the case of the valency of ferric iron. The vapour density indicated the formula Fe_2Cl_6 for ferric chloride, and the valency of the iron was therefore 3 by the first definition and 4 by the second definition, assuming that the two atoms of iron were directly linked together. More recent vapour density determinations however indicate that, at sufficiently high temperatures, the formula is $FeCl_3$.

It is of interest to notice that if the valencies of the elements are deduced from the composition of their highest oxides (by the first definition) we find elements with all valencies from 1 to 8.

E.g. Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, Cl_2O_7, OsO_4.

[The equivalent weight of the element is that weight of it which combines with eight parts of oxygen and dividing the respective atomic weights by these equivalent weights we obtain 1, 2, 3, 4, 5, 6, 7 and 8 respectively.]

But if we define the valency of the atom as the maximum number of atoms of *hydrogen* with which it can combine (or failing hydrogen, which does not unite with some elements, we can make use of the organic radicles such as methyl or ethyl) we find that the valencies are never greater than 4.

E.g. NaH, CaH_2, $Al(CH_3)_3$, SiH_4, PH_3, SH_2, ClH.

And now if we add together the highest valency deduced from the oxide and the highest valency deduced from the hydride (methide, etc.) we obtain, in many cases, 8. Thus Si gives, by the two definitions, 4 and 4, P 5 and 3, S 6 and 2, Cl 7 and 1. This remarkable circumstance has some theoretical importance.

48. "Unsaturated" compounds and "molecular" compounds. If we assume that each atom has a definite maximum valency we encounter certain difficulties. These difficulties may, to a large extent, be disposed of if we make certain assumptions, but in some cases they remain unexplained. Nitric oxide, NO, is a well-known offender, since however we deduce the valencies of nitrogen and oxygen we cannot get them to "fit."

If we find a compound in which the valency of one or more of the atoms is obviously less than its maximum value, we say that the compound is *unsaturated*. Thus, we know that the maximum valency of phosphorus is 5, yet we can obtain PCl_3 as well as PCl_5, so we say that the phosphorus in PCl_3 is unsaturated. Similarly, with ethylene, C_2H_4, and acetylene, C_2H_2. Now it *generally* happens that when the valency of an atom changes it does so by two units at a time, as seen in the examples quoted. Consequently we can imagine that the "latent" valencies satisfy one another, thus:

$$< P \begin{array}{l} \diagup Cl \\ -Cl \\ \diagdown Cl \end{array}$$
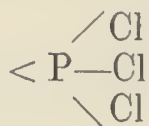
This circumstance, that the valencies change in pairs of units, was called the "law of even numbers" and was supposed to be universal. It was also expressed by saying that the valencies of any atom must be either odd or even but could not be both. There are however so many exceptions that the circumstance cannot be described as a law; it is remarkable however how often it holds true.

[Amongst the exceptions may be mentioned NO and NH_3; Cl_2O and ClO_2; $InCl_3$, $InCl_2$ and $InCl$; $GaCl_2$ and $GaCl_3$.]

We can generally ascertain at once whether a compound is unsaturated by ascertaining whether it will *combine directly* with a univalent element. Thus, ethylene and acetylene combine directly with bromine, whereas *saturated* compounds, such as methane and ethane, only react with bromine by *replacement*, hydrogen atoms being replaced by bromine atoms.

49. A more serious difficulty is encountered when a compound which appears from its composition to be saturated, is found to combine directly with something else. The maximum valency of silicon, for example, has

been fixed as 4 since its highest oxide is SiO_2 and its highest chloride is $SiCl_4$. But silicon fluoride, SiF_4, is found to combine directly with potassium fluoride, giving $SiF_4 . 2KF$. Similarly, barium chloride appears to be saturated, if we assume chlorine to be univalent, yet it combines directly with "water of crystallisation," giving $BaCl_2 . 2H_2O$. There are numerous cases of the same kind, and chemists, until a short time ago, were content to explain away the difficulty by assuming that compounds may be divided into two classes, namely, (1) atomic compounds in which the atoms are directly associated together by their valencies, and (2) molecular compounds, in which whole molecules combine together "somehow." In recent years many attempts have been made to improve upon this assumption; it has been suggested, for example, that in addition to the apparent maximum valency, each atom may possess "residual" valencies which come into play when whole molecules unite together. A much more definite and comprehensive theory has been developed by Werner; this theory, which has led to important new discoveries, gives a consistent explanation of the nature of the so-called molecular compounds*.

50. It is remarkable that although the theory of a fixed maximum valency is met with many difficulties in the domain of Inorganic Chemistry, the chemistry of carbon presents no difficulties of the same kind. If we assume that carbon is always quadrivalent (in terms of the second definition, above) we can satisfactorily account for the formulae of some hundreds of thousands of compounds. In cases also where the same formula may be arranged in different ways, we can predict how many (isomeric) compounds having this formula are capable of existing and this prediction agrees exactly with experimental results. Our formulae show, for example, that

* See *New Ideas on Inorganic Chemistry* by Werner. Translated by Hedley.

there should be only one kind of ethyl alcohol, $C_2H_5(OH)$, but two kinds of propyl alcohol, $C_3H_7(OH)$ and such is found to be the case. As many different ways in which we can arrange the formula so many compounds can exist. Numerous instances which were apparently in contradiction to this statement can be entirely explained if we assume that the valencies of the atoms must exert their influence in space of three dimensions and not merely in two, as we usually represent them in writing constitutional formulae on a plane paper. The formula for lactic acid, for example, is written, in one plane, as

$$\underset{\displaystyle \overset{|}{COOH}}{\overset{\displaystyle \overset{H}{|}}{CH_3-C-OH,}}$$
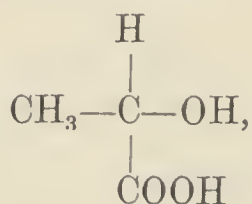
interchanging the position of the groups will make no difference, as such formulae are understood. If however we represent this formula in space of three dimensions, a carbon atom in the centre and the four groups, CH_3, OH, COOH and H, situated round it in positions corresponding with the four angles of a circumscribed tetrahedron, it will be evident that there are two ways in which the groups may be arranged; these are related to one another as an object to its mirror-image. A carbon atom directly associated with four different groups or atoms is called an asymmetric carbon atom. Compounds which contain one or more asymmetric carbon atoms when found in nature often have the power of rotating the plane of polarisation of light, sometimes to the right, sometimes to the left. Compounds which behave in this way are said to be "optically active" and are classed as "dextrorotatory" and "laevorotatory" accordingly. When compounds containing one or more asymmetric carbon atoms are prepared artificially, by synthesis, they are always optically inactive, but it is

then often possible to "resolve" them into two con-
stituents, one of which is dextrorotatory and the other, to
an equal degree, laevorotatory.

51. Relation between atomic weight and density.

Since volume $= \dfrac{\text{mass}}{\text{density}}$, we may call the ratio

$$\frac{\text{atomic weight}}{\text{density}}$$

the *atomic volume*.

Similarly $\dfrac{\text{molecular weight}}{\text{density}} = \text{molecular volume}$.

The number expressing this ratio will, of course,
depend on the units chosen. Taking the formula weight
in grams, we usually refer to the volume in cubic centi-
metres in the case of solids and liquids, and in units of
11·2 litres (at 0° and 760 mm.) in the case of gases. Thus
when we say that the atomic volume of lithium is

$$\frac{7}{\cdot 59} = 11 \cdot 8,$$

we mean that one atomic weight of solid lithium in grams
would fill 11·8 c.c.; but if we say that the molecular
volume of oxygen is 2 we mean that one molecular weight
of oxygen in grams will fill 22·4 litres at 0° and 760 mm.

Specific volumes * *of gases.* By definition (page 24) the
molecular volume of all gases must be 2 without exception,
assuming that the gas laws hold. The atomic volumes,
however, vary considerably. Thus the atomic volumes
of hydrogen, oxygen and nitrogen are 1 at all temperatures
so far investigated. Those of chlorine, bromine and iodine
are also 1 at moderate temperatures; that of iodine,
however, becomes 2 at sufficiently high temperatures, and
bromine, and perhaps chlorine, show a similar tendency.
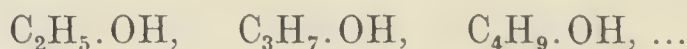The atomic volumes of phosphorus and arsenic at moderate

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* The term "specific volume" is used in Chemistry to mean

$$\frac{\text{formula weight}}{\text{density}}.$$

temperatures are $\frac{1}{2}$, but at very high temperatures approach to 1. Mercury, zinc, cadmium, silver, potassium and sodium all have the atomic volume 2. In the case of sulphur vapour, the value varies from about $\frac{1}{4}$ to 1 (or perhaps still greater) with rise of temperature.

[This is, of course, only another way of saying that the atomicity of hydrogen, oxygen, etc. is 2, of phosphorus and arsenic 4, of mercury, etc. 1, and of sulphur from 8 to 2 or less.]

52. Specific volumes of liquids. In the case of gases which obey the gas laws, it is evident that we are justified in comparing all the values in terms of the volume measured at a standard temperature and pressure, since all behave alike. With liquids however the expansion on heating is by no means regular, and it is of importance to determine the values at temperatures which are physically comparable. According to the theory of van der Waals, the values should be compared at temperatures which are *corresponding* (see page 18). It happens however that the boiling points of liquids at atmospheric pressure are approximately corresponding states, since the boiling points (absolute) are approximately $\frac{2}{3}$ of the critical temperatures. Most of the determinations of the specific volumes of liquids have been made at their boiling points and interesting results have been obtained. Thus, in a series of similarly constituted organic compounds, such as the alcohols

$$C_2H_5.OH, \quad C_3H_7.OH, \quad C_4H_9.OH, \ldots$$

or the acids

$$CH_3.COOH, \quad C_2H_5.COOH, \quad C_3H_7.COOH, \ldots,$$

each member of which differs in formula from the next by CH_2, the difference in molecular volume, at the boiling point, of each successive member is found to be 22 units. Again, in certain cases, when one carbon atom replaces two hydrogen atoms in the formula, there is no change of volume. Hence it is concluded that the specific volume

of $C = 11$ and that of hydrogen $= 5 \cdot 5$. Oxygen in alcohols and in water has the value $7 \cdot 8$, whereas oxygen in aldehyde or acetone has the value $12 \cdot 2$.

These numbers are obtained by assuming that the property is an *additive* one and that the volume of the group or element is equal to the difference between the molecular volumes of two compounds which differ in formula by that group or element, i.e., that the volume of the compound is equal to the sum of the volumes of its constituents. In many cases this is approximately true. Thus, if we take the above values for carbon, hydrogen and oxygen and *calculate* the molecular volume of acetic acid, we obtain $2 \times 11 + 4 \times 5 \cdot 5 + 7 \cdot 8 + 12 \cdot 2 = 64$.

[Since we know, from chemical considerations, that one of the oxygen atoms in acetic acid is singly linked, as in water, and the other is doubly linked as in aldehyde.] *Experimental* determination of the molecular volume of acetic acid gives $63 \cdot 8$.

In certain other cases however the agreement is not good, notably when the formula contains doubly or trebly linked carbon or a closed ring. This fact shows that the property is not strictly additive but *constitutive* also, i.e., it depends not only on the number and nature of the atoms, but also upon the way in which they are associated together. It must be observed also that the value of the atomic volume of an element when determined directly is, in most cases, different from that deduced from its compounds in the manner above indicated.

52 a. Atomic volumes may also be calculated for dissolved substances if we know the densities of the solution and solvent and concentration of the solution. Traube in this way deduced the following values: $C = 9 \cdot 9$, $H = 3 \cdot 2$, O (singly linked) $= 2 \cdot 3$, O (doubly linked) $= 5 \cdot 5$. If we calculate the molecular volume of a compound from these numbers, on the additive principle, the result is always smaller than the value directly determined from the compound itself. This difference has a constant value of about 26; it is called the molecular co-volume, and is supposed to represent the space in which the molecule moves or "the molecular domain." [Compare $(V - b)$ in van der Waals' formula.]

53. Specific volumes of solids. In contrast with gases and liquids, the change of volume of solids with temperature is so small that it may be practically left out of account; the determinations have usually been made at the ordinary temperature. The relationships here are more complicated than in the case of liquids, but the partly additive character is manifested by definite relationships in certain cases. It is found that the molecular volume of a solid compound is, as a rule, smaller than the sum of the volumes of its constituents; in some cases the molecular volume is less than the atomic volume of one constituent. In other cases the molecular volume is greater than those of its constituents, or may be approximately equal to them. Some of the relationships may be given in illustration. The volume of Cu_2O is the same as that of $2CuO$; if we assume the additive rule and suppose that the volume of the copper remains constant, it would appear that the oxygen occupies twice as much space in the first as in the second. The molecular volume of potassium chloride is 37·4 and that of potassium is 45·2. The molecular volumes of certain highly hydrated salts are equal to that of the water which they contain, taken as ice. In most of these cases it is evident that the method of subtracting the volume of one constituent, in order to deduce the volume of the other constituent, would give us absurd results. In potassium chloride, for example, the chlorine would occupy a negative volume!

Some definite relationships have been observed in the volumes of a series of salts of the same metal. Thus, the atomic volume of silver is 10·28 and the molecular volumes of silver oxide, chloride, bromide and iodide are 30·8, 25·8, 29·7 and 41·8 respectively. It will be seen that these numbers are all (either exactly or very approximately) equal to 5·14 multiplied by a whole number. This looks as if the silver has a "volume unit" or "stere" of 5·14, which appears to dominate the volume of all these silver salts. Similar relations are found in many other cases (Schröder).

If we compare the atomic volumes of the elements themselves, as directly determined, in the solid state, we notice that in some cases analogous elements have approximately the same atomic volume. [E.g., $Cl = 25 \cdot 0$, $Br = 25 \cdot 1$, $I = 25 \cdot 7$. In other cases they progressively increase, e.g., $Li = 13 \cdot 1$, $Na = 23 \cdot 7$, $K = 45 \cdot 5$, $Rb = 56$, $Cs = 71$.] Also that, generally, elements which have relatively large atomic volumes are more chemically active than those whose atomic volumes are small. Facts of this kind are at once apparent if we take the atomic weights as abscissae and atomic volumes as ordinates and trace a curve through the points so obtained (Meyer's atomic volume curve). In this way many other relationships become apparent. We see that the volume varies with the atomic weight in a *periodic* manner and that many physical properties, such as melting point and compressibility, vary in a similar way.

54. Volume and Valency. It has been observed that in many cases equivalent weights of different elements, when in combination with other elements, occupy equal volumes, or else, that the volumes stand to one another in a simple relation. Such observations have always been more or less indefinite and had no theoretical explanation. Barlow and Pope have recently developed a theory, however, which not only accounts for these facts, but shows in a very complete manner a connection between crystalline form and constitution. It is assumed that each atom occupies a definite space or "sphere of influence," that a solid crystal is made up of such spheres closely packed together, and that the volume of this atomic "domain" is proportional to the valency of the element. In terms of this theory, we can construct models which reproduce, in a remarkable way, the crystalline forms of numerous substances. A similar relationship is found also in the (liquid) paraffins at their melting points (Le Bas). If we take the molecular volume of any of these paraffins and divide it by the total number of valencies of the atoms present, we get the constant number $2 \cdot 97$. Thus the molecular volume of the hydrocarbon $C_{12}H_{26}$ is $219 \cdot 9$, and the total number of valencies is $12 \times 4 + 26 = 74$; the volume of $C_{24}H_{50}$ is 434 and the total valencies are $24 \times 4 + 50 = 146$.

If we calculate the value of the atomic volume of hydrogen and of CH_2 by subtraction, we get $H = 2 \cdot 97$ (mean value) and $CH_2 = 17 \cdot 83$. The atomic volume of carbon is therefore $11 \cdot 89$ and

the ratio $\dfrac{C}{H} = \dfrac{11\cdot89}{2\cdot97} = 4$ (almost exactly), i.e. the ratio of the valencies.

According to these determinations the molecular volume of a normal paraffin (C_nH_{2n+2}) at its melting point is $(6n + 2)\,2\cdot97$.

55. Refractive power. The index of refraction of a liquid for light of a particular wave-length is found to vary with the physical conditions, especially with its density. But Gladstone and Dale in 1858 showed that if n is the refractive index and d the density, the quantity $\dfrac{n-1}{d}$ alters very slightly with conditions of temperature, etc. In order to compare this quantity for different chemical substances, the value is multiplied by the formula weight. Thus $\dfrac{n-1}{d}$ multiplied by the molecular weight is called the molecular refractive power or molecular refraction; multiplied by the atomic weight, it is called the atomic refractive power or atomic refraction, and so on. It is written $\dfrac{n-1}{d}\,M$, where M is the formula weight.

A more complicated formula, but one which gives rather better results, was afterwards proposed on theoretical grounds, namely $\dfrac{n^2-1}{n^2+2}\dfrac{M}{d}$. Both of these formulae are in use; they may be written $(n-1)\,V$ and $\dfrac{n^2-1}{n^2+2}\,V$, where V is the molecular or atomic volume.

The molecular refraction, like the molecular volume, is to some extent an additive property, that is to say, the molecular refraction of a compound is often equal to the sum of the atomic refractions of its constituents, and the values for each constituent can then be obtained from a series of compounds by subtracting the difference, as was done in the case of atomic volumes. In this way, for light of a given wave-length (the red hydrogen line), the following values were calculated for the values of $\dfrac{n^2-1}{n^2+2}\dfrac{M}{d}$: $C = 2\cdot365$, $H = 1\cdot103$, O (in hydroxyl) $= 1\cdot506$, O (in aldehydes, ketones, etc.) $= 2\cdot328$.

If the property is additive, we can calculate from these numbers the values for compounds of these elements. Thus, for acetic acid the calculated value would be

$$2 \times 2\cdot365 + 4 \times 1\cdot103 + 1\cdot506 + 2\cdot328 = 12\cdot97.$$

This accords well with the values found by experiment. But it is found that the property is partly "constitutive"; the values are different, for example, according as carbon atoms are singly, doubly or trebly linked, and an open chain of carbon atoms has a different value to a closed ring.

56. Relations between atomic weight and properties. Periodic classification. Ever since Dalton's time, when definite numerical values were given to the atomic weights, chemists have been seeking to find relationships between the atomic weights and the general physical and chemical characters of the elements. Prout, in 1815, suggested the hypothesis that all matter was derived from a parent substance, "protyl," which might be hydrogen, and that all the atomic weights should therefore be simple multiples of the atomic weight of hydrogen. This hypothesis had to be modified when the atomic weight of chlorine was shown to be 35·5 and it was then suggested by Dumas that perhaps all the atomic weights were multiples of 0·5. The very exact determinations however which were subsequently made by Stas seemed to show that no such simple relation exists and the hypothesis was for the time abandoned. In recent years many very accurate determinations of atomic weights have been carried out and it is remarkable that, if they are calculated on the basis that the atomic weight of oxygen is exactly 16, many of them are practically whole numbers. This is one of the reasons why many chemists prefer this unit rather than H = 1, and Prout's hypothesis in various modified forms has to some extent been revived. Prout also drew attention to the fact that in certain cases elements closely allied in character (Fe, Co, Ni) had the same atomic weight, which was taken at that time as 28. Also that the atomic weight of nitrogen was just half of the number. This appears to be the first definite attempt to recognise a relationship between atomic weight and properties.

Döbereiner (1817) first pointed out that certain groups of three closely analogous elements have atomic weights which are in arithmetical progression. Amongst examples of this may be quoted Li, Na, K; Ca, Sr, Ba; Cl, Br, I; S, Se, Te. In each case it will be observed that the atomic weight of the middle element is, either exactly or very nearly, equal to the mean of the other two. Odling later attempted to arrange all the analogous elements

into groups and noticed some definite numerical relations between their atomic weights; more especially, he pointed out that in analogous elements there is frequently a difference of 4, or a multiple of 4, units in the atomic weights. This observation is of interest in view of recent theories (see Chapter IX).

No successful attempt had been made, so far, to include all the elements in one classification in the order of their atomic weights. De Chancourtois in 1863 suggested the outline of such a classification in a geometrical way and pointed out that the series of numerical characteristics had a resemblance to a sequence of musical sounds and to the bands and lines of the spectrum.

In 1864 Newlands put forward a much more definite and complete scheme, which clearly showed the periodic character of the change in properties with increasing atomic weight. He called this relationship the "law of octaves," since, with the elements then known, a repetition of general chemical character occurred at every eighth element. In 1869, Mendelejeff published an improved and amplified modification of this mode of classification and demonstrated its important applications. Lothar Meyer, in the same year, brought out his celebrated atomic volume curve, which has been mentioned above, and pointed out the periodic character of the relationship. The principle underlying this classification is called the *Periodic Law*. It states that the properties of the elements are periodic functions of their atomic weights.

An outline of the way in which the classification is tabulated may be given as follows:

Arrange the elements in a horizontal line on a strip of paper in the numerical order of their atomic weights, thus:

H	Li	Be	B	C	N	O	F	Na	Mg
1	7	9	11	12	14	16	19	23	24

Al	Si	P	S	Cl	K	Ca	Sc	....U
27	28	31	32	35·5	39	40	44	238·5

Consider now the elements Li, Be, B, C, N, O, F. We

find here a gradual change in properties from the well-marked electropositive element lithium to the strongly electronegative element fluorine. The next element in order is sodium, a strongly electropositive element closely allied to lithium. In fact, the general chemical characters of lithium are distinctly repeated in sodium. Similarly, the general chemical characters of beryllium are repeated in magnesium, those of boron in aluminium and so on. If therefore we cut off our horizontal list after fluorine and paste the succeeding strip underneath the first, so that Na falls below Li, each of the succeeding elements, up to chlorine, will fall under an element with which it is closely analogous.

On continuing this process we are met with some difficulties. We place K under Na and Ca under Mg, but, when the table was first constructed, there was no analogous element to place under Al. A vacant space was therefore left. Ti quite naturally falls under Si, V under P, and Cr under S. But the next element, which has to come under Cl, is *manganese*. It is, at first sight, impossible to reconcile this with chemical analogy; Mendelejeff however points out certain resemblances, such as the isomorphism of the perchlorates with the permanganates, which he considers sufficient to justify the inclusion of manganese in this place.

The next element on our list is copper; another alkali metal, analogous to potassium, is not found until rubidium, whose atomic weight is 85·5. If however we place copper under potassium, that is to say, if we continue our process of arrangement in strictly numercial order, other elements will fall in their proper places, e.g., Zn under Ca, As under V and Se under Cr. (Spaces originally occurred under Se and Ti.) We must, in this case, try to justify the inclusion of copper with the alkali metals. No strict analogy really exists; it may be remarked however that copper in the cuprous state is in some respects very analogous to silver, and silver can replace potassium, isomorphously, in alum. But this

argument does not amount to much, since one might include mercury for similar reasons.

In continuing the construction of the Table, several other cases of this kind occur, where we are obliged to classify certain elements together, which, in a practical sense, show little or no analogy. Nevertheless, such difficulties may usually be "explained away."

The elements Fe, Co, Ni; Ru, Rh, Pd; and Os, Ir, Pt have to be classified apart in order to preserve the symmetrical arrangement of the Table. These nine elements, which have certain general chemical characters in common, are conveniently arranged in three sub-groups of three closely allied elements which differ only slightly in atomic weight.

Omitting, for the present, the non-valent elements and most of the rare-earth elements, the table of the elements classified in accordance with the Periodic Law may be presented in the following form. Spaces are left in certain places in order that the arrangement may be symmetrical; many of the spaces originally left have already been filled by newly discovered elements (see below). The horizontal lines are called *series* and the vertical columns *groups*.

	I	II	III	IV	V	VI	VII	VIII
1	(H)							
2	Li	Be	B	C	N	O	F	
3	Na	Mg	Al	Si	P	S	Cl	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni
5	Cu	Zn	Ga	Ge	As	Se	Br	
6	Rb	Sr	Y	Zr	Nb	Mo		Ru Rh Pd
7	Ag	Cd	In	Sn	Sb	(Te)	I	
8	Cs	Ba	La	Ce				
9								
10					Ta	W		Os Ir Pt
11	Au	Hg	Tl	Pb	Bi			
12		Ra		Th		U		

57. Some of the principal features of the Table, which deserve particular attention, are the following:

(*a*) In each *group*, the metallic or electropositive character of the element, as a general rule, becomes more pronounced as the atomic weight increases; whereas in each *series* the metallic character gradually diminishes as the atomic weight increases, from the first to the seventh member. Elements situated in the middle part of the series show less marked electronegative or electropositive character.

(*b*) The *valencies* of the elements as deduced from the composition of their highest *salt-forming* oxides [by definition 1, page 91] are the same for each group, whereas in each series they occur in the order: 1, 2, 3, 4, 5, 6, 7, 8. If however we deduce the valencies from the composition of the hydride (or methide, ethide, etc.) the order is: 1, 2, 3, 4, 3, 2, 1 for the first seven elements. In the eighth group we cannot determine the valency this way, but recently the compounds OsF_8 and $OsCl_8$ have been isolated, thus confirming the octavalency of an element of this group. [The position of the non-valent elements will be considered below.]

(*c*) If we number the series in the usual manner as is done in the given Table, we see that, to a large extent at any rate, we may divide the elements of each group into two sub-groups, classifying the elements together which belong to the *odd* and *even* series respectively. For example, in group II there is evidently very close chemical analogy between Ca, Sr, Ba, all members of even series; also between Mg, Zn, Cd, all members of odd series; but there is less direct resemblance between members of even and odd series, e.g. between Ca and Zn.

This subdivision unfortunately fails in some cases, notably in the *first* members of the groups which are nearly always in the wrong order. Thus C should obviously be sub-grouped with Si, N with P and O with S, but in each case the series are even-odd.

(*d*) The elements Cu, Ag, Au which are grouped with

the alkali metals evidently form a connecting link between the first and last groups; thus copper shows many analogies with nickel, silver with palladium. and gold with platinum.

(e) *The position of hydrogen.* It would at first sight appear that hydrogen should be included amongst the alkali metals, as it is represented in the given Table. This seems to be supported by the close analogy between acids and their alkali-metal salts. Hydrogen however has now been isolated in the solid state and it shows no metallic properties whatever. Moreover, the definite hydrides of Li, Ca, etc. are salt-like, whereas if hydrogen were a metal they should be alloys. Masson suggests that it would be preferable to consider hydrogen as the first member of the *halogen* family, and there is much to be said in favour of this view, which however seems to be repugnant to most chemists.

(f) *The position of the non-valent elements* (helium group). These elements, which have properties so distinct from any of the other elements, must, of course, be placed in a group by themselves and, in numerical arrangement of the Table, if we exclude the iron group, they would naturally fall between the halogens and the alkali metals.

			He	4		Li	7
F	19	....	Ne	20	....	Na	23
Cl	35·5	....	A	40	....	K	39·1
Br	80	....	Kr	81	....	Rb	85·4
I	127	....	X	128	....	Cs	133

If now we can bring ourselves to regard hydrogen as a member of the halogen group, the vacant space at the top of the first column will be suitably filled up.

Note that a discrepancy occurs in the strict numerical arrangement, since argon comes on the wrong side of potassium. The difference is slight and *might* be due to experimental error.

(g) *The position of tellurium.* Here the numerical arrangement of the Table has been deliberately falsified,

tellurium being placed before iodine. A very large number of re-determinations of the atomic weight of tellurium have been made in recent years, in hopes of clearing up this discrepancy, but, so far, without success. [It is worth remarking that the difference between the atomic weights of succeeding elements varies considerably, but in this region of the Table the difference is generally very small, and it has been suggested that the cause of the difference, whatever it is, might even produce a change of sign! It may be that the position of an element in a table depends upon some property which is approximately proportional to the atomic weight rather than on the atomic weight itself.]

(*h*) *The position of the "rare earth"* metals is a matter of some difficulty. A large number of these which are closely allied have atomic weights between about 140 and 180, being usually regarded as trivalent. Evidently they cannot be included in order of their atomic weights so as to fit in to the Table. They are therefore generally grouped together (as are the elements Fe, Co, Ni, etc.) and assigned a place somewhere between barium and tantalum. The properties of these elements vary very slightly from one member to the next and their separation is, consequently, difficult and their elementary nature is in some cases doubtful.

(*i*) *Numerical relations*. Some more or less definite numerical relations exist between the atomic weights of certain closely allied elements as was indicated above. But no formula has yet been discovered which gives a wholly satisfactory connection between the atomic weight of an element and its position in the table, although numerous attempts have been made in this direction by Mills, Carnelly, Vincent, Rydberg and others.

The differences between the atomic weights of consecutive elements are very irregular; but if we number the elements in the order in which they occur in the list and divide the atomic weight by this number there is much more constancy. The value of this ratio for a

large number of elements lies between about 2·3 to 2·7. A remarkable regularity is at first observed if, omitting hydrogen and including the non-valent elements, we add together the atomic weights of the first and last members of a series.

<p style="text-align:center">He Li Be B C N O F.</p>

We see that He + F, Li + O, Be + N, and B + C are all equal to 23, the atomic weight of Na. Continuing this up to chlorine we get a similar result although the numbers are not so good; thus,

He + Cl, Li + S, Be + P, B + Si, C + Al, N + Mg, O + Na, and F + Ne all = (nearly or exactly) 39, the atomic weight of K.

58. Uses of the Periodic Classification. (1) The correction of doubtful atomic weights. If we happen to have selected the wrong multiple of the equivalent weight as the atomic weight, the periodic table at once reveals the fact, since the element will fall out of its proper relationships. Notable cases in which this principle has been successfully applied are those of beryllium, indium and uranium. In these cases wrong numbers had been universally accepted on what was afterwards shown to be insufficient evidence. Mendelejeff pointed out the impossibility of reconciling these values with the periodic classification and this stimulated chemists to re-determine the true values. Similar considerations led to the re-determination of the exact equivalent weights of gold, platinum, osmium and iridium with the result that the accepted values were considerably modified.

(2) As a method of predicting the existence of hitherto undiscovered elements. Blank spaces were found, for example, where we now place the elements gallium and germanium. These elements were not only predicted by Mendelejeff, but he foretold their properties. Gallium was subsequently discovered by Lecocq de Boisbaudran and germanium by Winkler, and the

properties of these elements coincided in a remarkable way with Mendelejeff's prediction.

(3) As the most comprehensive means of classification of the elements. Notwithstanding its important application for this purpose it must be remembered that, from a purely chemical standpoint, the classification is by no means a perfect one. The classification, for example, of manganese with the halogens, and of copper and gold with the alkali metals, is repugnant to the feelings of the practical chemist and is not consistent, since the highest salt forming oxide of copper is CuO and of gold Au_2O_3. It is evident that if this mode of classification were employed in teaching beginners the general chemical characters of the elements, they might be seriously misled in certain cases.

CHAPTER V

CHEMICAL CHANGE

59. The essential characteristic of a chemical change is that the properties of the product, or products, found at the end of the change ("resultants") should be different from those of the substances started with ("reactants"). In terms of the molecular theory, the essential characteristic is that the original molecules disappear wholly or (more usually) in part, whilst molecules having a different composition make their appearance. Definitions of this kind, however, must not be pushed too far. As a matter of fact, it is, in some cases, very difficult to say whether a change should be classed as physical or chemical. The vaporisation of water, for example, is universally regarded as a purely physical change, yet there is no doubt that liquid water contains molecules more complex than those in water vapour. Some attempt to distinguish between the two cases by saying that the chemical change is permanent whilst the physical change is temporary, and they illustrate this by reference to a heated platinum wire which regains its original properties when cooled, and a mixture of iron and sulphur which, on heating, gives a new substance. But this distinction would not apply to cases of reversible dissociation, which are always regarded as "chemical" processes. The distinction between the two classes is a useful one and in most cases presents no difficulty, but it must not be regarded as absolute.

Reversibility of chemical changes. In the ordinary way of writing chemical equations the reaction is represented as going entirely one way or the other; the substances on the left-hand side, or reactants, being completely transformed into the resultants. In our common analytical operations, for example, we write:

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$$

and $$NaOH + HCl = NaCl + H_2O,$$
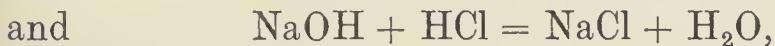
and, as far as our ordinary quantitative methods can tell us, these representations would appear to be quite correct. When however we mix, say, hydrocyanic acid and caustic soda in equivalent quantities, it is evident that this mode of representation is not sufficient, for the resulting solution can easily be shown to contain both the substances with which we started and, presumably, a new substance, potassium cyanide, which we obtain on evaporation. Similarly, when we precipitate a solution of a metal of the second group as sulphide by passing H_2S, the change generally appears to be a quantitative one. Yet many of these metallic sulphides when heated with HCl yield H_2S. In such cases it is now usual to write the equation with the "double arrow" sign in place of the equality sign: e.g.,

$$2SbCl_3 + 3H_2S \rightleftarrows Sb_2S_3 + 6HCl,$$

to show that the reaction can be made to go either way, i.e. that it is *reversible*.

Probably all chemical changes should, strictly, be regarded as reversible, although it is the custom to call them *irreversible* if the change can be actually demonstrated practically in one direction only. [As examples, consider the preparation of oxygen from potassium chlorate, or of nitrous oxide from ammonium nitrate.] Theoretically then, at the end of all chemical changes, in which nothing is removed from the sphere of action, it may be supposed that the final product is a mixture of reactants and resultants; in so-called irreversible changes

the proportion of the reactants existing in the final mixture is too small to be detected.

Since when the change is entirely finished the reactants and resultants co-exist, it is evident that they must be in equilibrium with one another; hence the expression "*chemical equilibrium*." It must be supposed in terms of the kinetic theory that this equilibrium is a mobile and not a static one, i.e. that both the forward and reverse actions are continually going on, but that the amount of change in a given time is the same in both directions, i.e. that they balance one another; hence the term *balanced action*.

The term *dissociation* is applied to any *reversible* chemical change in which a compound splits up into two or more parts, or in which the more complex molecule resolves itself into simpler ones. If the change is not practically reversible it is simply called *decomposition*. Thus the changes

$$CaCO_3 \rightleftarrows CaO + CO_2, \qquad NH_4Cl \rightleftarrows NH_3 + HCl,$$
$$N_2O_4 \rightleftarrows 2NO_2, \qquad 2NO \rightleftarrows N_2 + O_2,$$
$$2HI \rightleftarrows H_2 + I_2, \qquad 2O_3 \rightleftarrows 3O_2, \qquad I_2 \rightleftarrows 2I$$
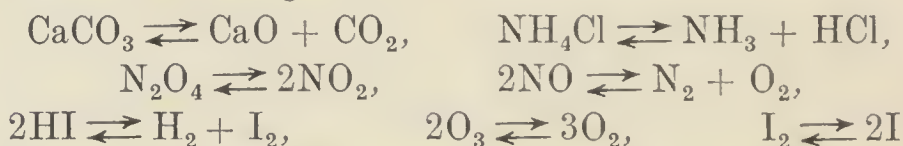
are examples of dissociation, whereas the changes

$$2KClO_3 = 2KCl + 3O_2, \qquad NH_4NO_3 = 2H_2O + N_2O,$$
$$CaC_2O_4 = CaCO_3 + CO, \quad 2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

would be classified as decompositions.
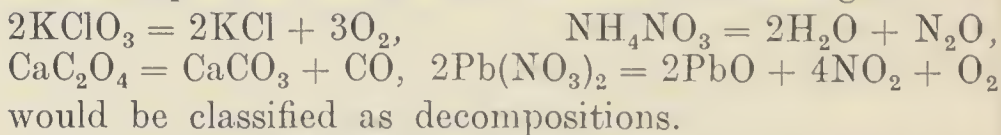
The term *electrolytic dissociation* is employed for those reversible changes in which the molecule of an electrolyte reversibly splits up into two or more electrically charged parts (see Chapter VII).

60. Conditions and circumstances which influence chemical change. The most important conditions by which chemical changes are affected are (1) the *concentrations* of the reacting substances, (2) the *temperature*, (3) the *pressure*. In many cases we have also to consider the influence of *catalytic agents* and also of *light*.

I. *The influence of concentration. Law of Mass Action.* [The word concentration is used here in the

sense explained on page 33, i.e. it is the number of molecules in unit volume.] The rate at which a chemical change takes place is, in most cases, measured by the change in concentration which occurs in a given time*, i.e.

$$\text{rate} = \frac{\text{change in concentration}}{\text{time}}.$$

The law of "Mass Action" states, in effect, that this *rate is directly proportional to the concentration*; if more than one molecule takes part in the change, the rate is directly proportional to the *product of the concentrations*. For one molecule reacting, we can express this by saying that the rate = concentration × a constant. For two molecules reacting, the

rate = product of the two concentrations × a constant.

The rate of chemical change is continuously changing and it is therefore necessary to specify the instant at which the rate is measured. We speak of the rate *at a time t*. We cannot directly measure this, as the rate changes so quickly. We can however determine the change of concentration which takes place at intervals of, say, two or three minutes, and from this, with the aid of mathematics, we can calculate the rate *at a given instant*.

60 a. Mathematically, we express the rate of chemical change as $\dfrac{dx}{dt}$, where dx is the quantity changed and dt the time interval, both dx and dt being infinitely small quantities.

In reactions in which only one molecule takes part in the change it is found that the rate of change at any instant is directly proportional to the concentration of the reacting substance at that time. Thus, if A is the original concentration and x is the quantity changed during the time interval, $A - x$ is the concentration remaining. Then

$$\frac{dx}{dt} = K(A - x) \quad \dotsc\dotsc\dotsc\dotsc\dotsc\dotsc(1)$$

$$\left[\text{or } K = \frac{1}{t} \log_e \frac{A}{A - x} \right].$$

---

* In speaking of the rate of change in a *solid*, we refer to the change in total quantity taken. Compare Section 108.

K is called the "velocity" constant. It depends on the nature of the reaction and the temperature. [Also on the nature of the medium, etc.]

If two molecules take part in the change the rate is proportional to the *product* of the concentrations; if the substances react in equal molecular ratio, the rate is expressed by

$$\frac{dx}{dt} = K (A - x)^2 \quad \dots\dots\dots\dots\dots(2)$$

$$\left[\text{or } K = \frac{1}{t} \frac{x}{A (A - x)} \right].$$

If three molecules take part in the change and act in equal molecular ratio, the rate is

$$\frac{dx}{dt} = K (A - x)^3 \quad .. \quad \dots\dots\dots\dots\dots(3)$$

and so on.

Examples of such reactions are

(1) $NH_4NO_3 = 2H_2O + N_2O$,

(2) $CH_3COOEt + NaOH = CH_3COONa + EtOH$

and (3) $3HCNO = H_3C_3N_3O_3$.
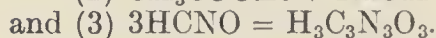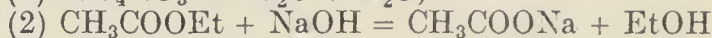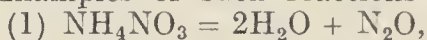
A reaction of the first type is called a reaction of the *first order*, and, generally, a reaction the rate of which is expressed by the relation $\frac{dx}{dt} = K (A - x)^n$ is called a reaction of the nth order.

Theory assumes that when n molecules take part in a change the action will be of the nth order. Hence these reactions are often spoken of as "unimolecular," "bimolecular" and so on. In many cases experiment shows that this is the case; i.e. the order of the reaction is found to be the same as the number of molecules which are represented by the chemical equation as taking part in the change. There are, however, numerous exceptions. Most gaseous reactions, for example, are found to be of the first order, even though the chemical equation indicates the reaction of several molecules. Probably in these cases the reaction really takes place at the *surface* of the containing vessel only, and the rate which is actually measured is the rate of diffusion of the gas towards the surface. In other cases, where exceptions occur, it is assumed that the changes take place in stages and that only the slowest change is actually measured.

If the change is a reversible one, it is evident that the results will be complicated by the fact that both the forward and reverse changes are taking place at the same time; the rate actually measured in such cases is really the *difference* between the two rates.

61.   When the system comes to equilibrium, it must be supposed that these two rates balance one another. Since each rate may be represented as the product of the concentrations into a constant, we shall have, for a reaction in which only one molecule takes part, either way,

$$kC = k'C',$$

where C and C' are the concentrations of the reactant and resultant respectively in the final equilibrium mixture.

If two molecules take part in the change in equal molecular concentration producing two new molecules,

$$kC^2 = k'C'^2.$$

Generally, when the change consists in the action of n_1 molecules of A on n_2 molecules of B producing n_3 molecules of C and n_4 molecules of D, and the concentrations at equilibrium are C_1, C_2, C_3 and C_4 respectively, we shall have

$$kC_1{}^{n_1}C_2{}^{n_2} = k'C_3{}^{n_3}C_4{}^{n_4}.$$

Note therefore that the power to which each concentration is raised denotes the number of molecules which take part in the reaction, i.e. the number which we have to put *before* its formula in the chemical equation.

The law of mass action for any number of substances reacting is generally written

$$\frac{k}{k'} = K = \frac{C_1{}^{n_1}C_2{}^{n_2}\ldots}{C_3{}^{n_3}C_4{}^{n_4}\ldots},$$

K being called the *reaction constant*.

[It is evident that the term *mass* action is somewhat misleading; it would be better to use the word *concentration*.]

We see from the above that the concentration of the reacting substances influences not only the *rate* of the reaction but also the *relative proportions* of the resultants and reactants in the final equilibrium mixture. We may investigate the matter experimentally in either way.

In measuring the rate, it is simplest to deal with irreversible changes; but in the case of reversible changes the initial rate may often be measured before the influence of the reverse change becomes appreciable. The reacting mixture is kept at a constant temperature and small measured volumes of it are taken out and analysed at definite time intervals. In some cases the rate may be determined by observing some physical property of the mixture. In a gas which dissociates with change of volume, for example, we can follow the rate of change in a closed vessel by observations of the pressure. In solutions of optically active substances, like sugar, rate may be determined by observing the change in rotatory power.

62. In order to investigate the law of mass action by the determination of the final concentrations of reactants and resultants when *equilibrium* is attained (sometimes called the statical method) we must, of course, keep the mixture at a definite temperature until no further change takes place. Its composition is then ascertained either by chemical analysis, under appropriate conditions, or by determination of some physical property. A few examples will be given in illustration.

In the reactions

$$N_2O_4 \rightleftarrows 2NO_2, \qquad PCl_5 \rightleftarrows PCl_3 + Cl_2$$

or
$$NH_4Cl \rightleftarrows NH_3 + HCl,$$
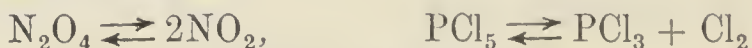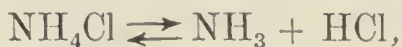
we can estimate the composition of the final equilibrium mixture by observing the density. But in the case of the reaction $2HI \rightleftarrows H_2 + I_2$ there is no change of volume and consequently the density would tell us nothing. In this case we *quickly cool* the mixture and analyse it (by titration with thiosulphate, or by measuring the free hydrogen, after shaking it with a solution of potassium iodide). The change, in either direction, at the ordinary temperature is so slow that the analysis can be completed before any appreciable change of com-

position takes place. In the case of reactions taking place in solution, it is evident that analysis of the equilibrium mixture by titration or by precipitation is, as a rule, inadmissible, since, in such operations, one of the products is removed from the sphere of action and the equilibrium is thus destroyed, with the result that the proportions alter. Thus, if we wished to investigate equilibrium mixture resulting from the reaction $AsCl_3 + 3H_2O \rightleftharpoons As(OH_3) + 3HCl$ it would be useless to attempt to titrate the free acid by means of standard alkali, because the neutralisation of the HCl would destroy the equilibrium and a further change in the forward direction would immediately follow. It happens however that there are some reactions in which such a method can be applied owing to the extreme slowness with which the changes take place at the ordinary temperature. A well-known instance of this is the reaction between alcohols and acids, known as *esterification*:

$$ROH + HX \rightleftharpoons RX + HOH$$
alcohol   acid   ester   water.
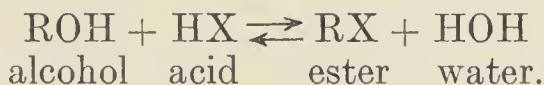
These esters react with water to produce alcohol and acid; but the process is usually so slow at low temperatures that it is quite safe to titrate the free acid, e.g. with baryta water. If therefore we start with known quantities of acid and alcohol and allow the mixture to come to equilibrium (say at 100°), then cool to the ordinary temperature and estimate the free acid by titration, we know the proportions of all the four constituents of the mixture.

This change has been extensively studied and the results have been of much service in establishing the truth of the law of mass action and of other important principles.

If we start with one gram molecule each of alcohol and acid, and if V is the volume of the resulting mixture, the concentrations, to start with, are $\dfrac{1}{V}$ of alcohol and $\dfrac{1}{V}$

of acid. When the change is completed, a certain quantity, say x molecules, of each of these constituents has been transformed into ester and water. The equilibrium mixture will therefore contain $1 - x$ molecules of acid, $1 - x$ of alcohol, x of ester and x of water. According to the law of mass action, therefore,

$$k \frac{1-x}{V} \times \frac{1-x}{V} = k' \frac{x}{V} \times \frac{x}{V},$$

or
$$K \left(= \frac{k}{k'} \right) = \frac{x^2}{(1-x)^2}.$$

By titration with alkali, in the way above indicated, we can find x and so calculate the value of K. Once we know this reaction constant we can predict what the result will be when we mix the substances in different proportions.

Note that in the above relation the V's cancel, i.e. the extent to which the reaction proceeds is *independent of the volume*. The same is true of the reaction

$$2HI \rightleftarrows H_2 + I_2.$$

But in the reactions

$$PCl_5 \rightleftarrows PCl_3 + Cl_2 \quad \text{or} \quad NH_4Cl \rightleftarrows NH_3 + HCl,$$
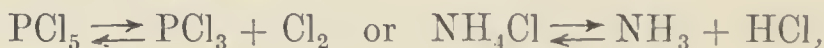
this is not the case.

Thus if we start with one molecule of PCl_5 and heat its vapour to a suitable temperature a certain quantity of it, say x molecules, will dissociate. If V is the volume of the equilibrium mixture, we shall have

$$k \frac{1-x}{V} = k' \frac{x}{V} \times \frac{x}{V},$$

or
$$K \left(= \frac{k}{k'} \right) = \frac{x^2}{(1-x)\,V}.$$

Evidently here if the volume is larger x must be larger, and conversely; if therefore we vaporise our PCl_3 in a smaller vessel, less of it will dissociate, at a given temperature.

63. If, in a chemical change, one or more of the reacting substances is *solid*, it appears difficult at first sight to understand how the law of mass action can be applied. It must be remembered however that the composition of the solid phases, unlike the liquid and gaseous phases, does not alter as the change proceeds, and we may therefore say that *concentration of a solid is constant*. The value of this constant can be included in the value of the reaction constant; thus, in the case of the change $CaCO_3 \rightleftharpoons CaO + CO_2$, if we call the concentrations of the three substances C_1, C_2 and P respectively, we shall have, in terms of the law,

$$kC_1 = k'C_2P,$$

or
$$K \left(= \frac{k'}{k}\right) = \frac{C_2P}{C_1}.$$

But since K, C_1 and C_2 are all constant we may write

$$K = P,$$

i.e. for a given temperature, the concentration of the CO_2 is constant. Experiment shows that this is the case (see Section 26).

Similarly in the change $3Fe + 4H_2O = Fe_3O_4 + 4H_2$ if we represent the concentrations of the four substances by C_1, P_1, C_2 and P_2 respectively, we have $K = \dfrac{C_2P_2{}^4}{C_1{}^3P_1{}^4}$, or since K, C_1 and C_2 are all constant, $K = \dfrac{P_2{}^4}{P_1{}^4}$, i.e. the ratio of the concentrations of hydrogen and water vapour must be constant, for a given temperature; this also can be proved by experiment.

II. **64.** *Influence of temperature on chemical change.* Both the *rate* of chemical change and the *final state of equilibrium* (i.e. the relative proportion of reactants and resultants) depend on the temperature. In a reversible change, the system comes to equilibrium when the rate of the forward change is equal to that of the reverse

change; if therefore alteration of temperature shifts the position of equilibrium, we must suppose that this is due to the fact that the rate of one of the changes is influenced more than that of the other; if alteration of temperature influenced both changes alike, the position of equilibrium would not alter. From this point of view the influence of temperature on chemical change may be regarded as solely due to change of rate.

Practically however it is most important to distinguish between the *initial* rate and the final position of equilibrium. In several cases serious mistakes have been made in confusing the increase of rate at which a given result is arrived at with the shifting of the point of equilibrium.

A few examples may be cited in illustration.

A mixture of oxygen (1 volume) and hydrogen (2 volumes) appears to be quite stable and remains apparently unchanged at the ordinary temperature for years. On sufficiently raising the temperature, the mixture explodes and water is formed. At first sight this looks as if the change $2H_2 + O_2 = 2H_2O$ was favoured by rise of temperature. We can easily prove however that the contrary is the case. The explanation is, that the oxyhydrogen mixture is really in the process of reacting all the time even at the ordinary temperature, but the rate is so extremely slow that it cannot be observed experimentally. The result of raising the temperature is to increase the *rate* at which the system comes to its true state of equilibrium.

Similarly, if oxygen is "ozonised" in the ordinary way in the laboratory, we obtain a mixture of ozone and oxygen containing perhaps 3 or 4 per cent. of ozone. If we pass this mixture through a heated tube all the ozone appears to be reconverted into ordinary oxygen. This would appear to indicate that raising the temperature destroys the ozone, i.e. that the change $3O_2 = 2O_3$ should be favoured by lowering the temperature. But experiments have proved that the contrary is the case;

oxygen can be partly converted into ozone merely by heating it to a very high temperature and the higher the temperature the greater is the proportion of ozone. We must consider therefore that our ozonised oxygen, containing 3 or 4 per cent. at the ordinary temperature, is an unstable, or metastable, mixture; the true equilibrium mixture at this temperature probably contains a quantity of ozone which is much too minute to be detected. The effect of raising the temperature has been to increase the *rate* at which the system comes to its true position of equilibrium.

The influence of temperature on the *rate* of a given chemical change is usually very great and increase of temperature always *increases* the rate. An increase of temperature of 10° often doubles or trebles the rate of reaction.

An apparent exception to this is sometimes found in the rate of transformation of a substance capable of existing in two forms, when there is a transition point (page 7). The rate of transformation of white tin into grey tin, for example, increases as the temperature falls below the transition point down to a certain temperature beyond which it decreases again. This is due to the fact that the white modification becomes more unstable the further it is cooled below the transition point and the less stable it is the quicker it changes; but this effect is after a time counterbalanced by the decrease of rate of change with decrease of temperature.

65. The influence of temperature on the final *position of equilibrium* is most important. In a reversible reaction, there is, for any given temperature, a definite ratio between the reactants and resultants when equilibrium is attained. If now the temperature is altered there will (in nearly all cases) be a shifting of this point, i.e. the proportions will alter. [This might be expressed shortly by saying that the value of K in the mass action formula depends on the temperature, with one or two exceptions.]

The question arises, which way will the given reaction be shifted by an alteration of temperature, assuming that the *volume is kept constant*? A simple rule (sometimes called *van't Hoff's principle of mobile equilibrium*) at once answers this question:

If the reaction (at constant volume) is attended with *absorption* of heat, *raising* the temperature will favour it, and conversely.

Chemical changes are classified as *exothermic* and *endothermic* according as heat is evolved or absorbed in the reaction. In a reversible reaction the two opposing changes are usually of opposite sign: one is attended with evolution of heat and the other with absorption of heat. Van't Hoff's principle therefore states, in effect, that raising the temperature shifts the equilibrium in the direction of the endothermic change and lowering the temperature shifts it in the direction of the exothermic change. As examples: The dissociation of calcium carbonate is an endothermic change and the combination of carbon dioxide with lime is an exothermic change; hence the equilibrium in the system

$$CaCO_3 \rightleftarrows CaO + CO_2$$
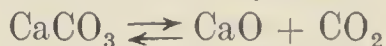
is shifted in the forward direction (left to right) by increasing the temperature. In the reactions

$$N_2 + O_2 \rightleftarrows 2NO \quad \text{and} \quad 3O_2 \rightleftarrows 2O_3,$$
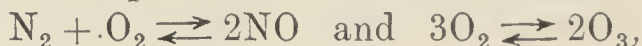
the forward changes are endothermic and the reverse changes are exothermic; hence the proportions of nitric oxide and of ozone respectively increase as the temperature is higher.

There are some changes in which the thermal value of the reaction is practically nil, i.e. heat is neither evolved nor absorbed. In such cases alteration of temperature makes no difference in the position of the final equilibrium. The esterification of ethyl alcohol by acetic acid, referred to above, is a well-known example of this; in the final equilibrium mixture, when the two substances react in equal molecular proportions, about $\frac{2}{3}$ of the alcohol is converted into ethyl acetate and this is found to be practically the same whether the operation is carried out at ordinary temperatures or at higher temperatures up to 220°. The *rate* at which this equilibrium state is arrived at of course varies enormously with

temperature; at ordinary temperature it is a matter of years, whereas at 220° equilibrium is attained after 24 hours.

III. **66.** *Influence of pressure on chemical change.* Pressure, like temperature, may influence both the rate at which a given change takes place and, in a reversible reaction, the position of equilibrium in the final equilibrium mixture.

The effect of pressure in changing the *rate* of a reaction is especially noticeable in gases whether the reaction is accompanied by change of volume or not. It is evident that this must be so since increase of pressure increases the concentration of the reacting substances.

As regards the *position of equilibrium,* i.e. the proportion of resultants to reactants when equilibrium is attained, the rule is quite simple. If the reaction is attended by diminution of volume it will be favoured by increased pressure, and conversely. Further, if the reaction is one in which no change of volume occurs, pressure makes no difference. Thus, in a reversible reaction of the type $A \rightleftarrows B$, if the volume of B is less than that of A, increase of pressure will shift the equilibrium in the forward direction, i.e. the equilibrium mixture obtained will contain a larger proportion of B than it did before.

In the case of gaseous reactions the influence of pressure is at once apparent from the "mass action" formula (Section 60), assuming, of course, that the temperature is kept constant. In the reaction $PCl_5 \rightleftarrows PCl_3 + Cl_2$, for example, the formula gave

$$K = \frac{x^2}{(1 - x)\,V}.$$

We see from this that if the system is in equilibrium at a pressure P and we now increase the pressure, V will diminish; the result will be that x must diminish also in order to restore equilibrium.

But in the reactions

$$2HI \rightleftarrows H_2 + I_2 \quad \text{or} \quad N_2 + O_2 \rightleftarrows 2NO,$$

the volume cancels, i.e. increase of pressure will affect each side of the equation alike; the position of equilibrium is therefore unaffected by pressure.

In solids and liquids the same rule applies, but the volume changes are usually very small for considerable alteration of pressure. Examples have already been mentioned (see Sections 5 and 16).

67. *The Rule of Le Chatelier.* The influence of temperature, pressure and concentration on the position of equilibrium is easily remembered by this simple rule, which states that if a system which is in equilibrium is subjected to a constraint (i.e. if one of these factors upon which the equilibrium depends is altered) the position of equilibrium will be shifted in such a direction as to oppose the constraint. Van't Hoff's principle of mobile equilibrium is a special case of the application of this rule. Thus, if we have the system $PCl_5 \rightleftarrows PCl_3 + Cl_2$ in equilibrium at a certain temperature, in a closed vessel, and then *raise* the temperature, the system will shift itself in such a way as to oppose the rise of temperature; that is to say, a change involving *absorption* of heat will take place. The only possible changes here are the formation and dissociation of the pentachloride, these changes being exothermic and endothermic respectively.

Similarly, if we have this system in equilibrium at a constant temperature and at a given pressure and we now *increase* the pressure, the system will shift itself in such a manner as to *lessen* this increase of pressure; i.e. the reaction will proceed in the direction in which the volume diminishes, namely the combination of the trichloride with chlorine.

The changes of melting point and of transition point with alteration of pressure, referred to in Section 4, afford further illustrations.

68. Le Chatelier's rule is a statement of a general principle which applies to both chemical and physical changes. It enables us to predict, in a qualitative way, the direction in which the equilibrium will be shifted when the conditions are altered. The application of thermodynamics enables us to go farther and to calculate not only the direction but also the amount of the change. Consider for the sake of simplicity a reversible reaction of the type $A \rightleftarrows B$. If C_1 and C_2 are the concentrations of A and B respectively, when the system is in equilibrium at a given (absolute) temperature T_1, the law of mass action states that $kC_1 = k'C_2$ or $\dfrac{k}{k'} = K_1 = \dfrac{C_2}{C_1}$, where K_1 is the equilibrium constant at T_1. If now the temperature is altered to T_2, the equilibrium will (in nearly all cases) be shifted; we shall have a new value for the equilibrium constant; call this K_2. Now the change of A into B is (in nearly all cases) attended with either evolution or absorption of heat. Let the quantity of heat involved in the change of one mol of A into B be denoted by Q if heat is *evolved* in the change and by $- Q$ if heat is *absorbed*. Then it can be shown from thermodynamical considerations that

$$\log K_1 - \log K_2 = \frac{Q}{2}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

Since, in our example, T_2 is greater than T_1, it is evident that the quantity $\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$ is positive; hence if Q is positive, K_1 must be greater than K_2—and conversely. If therefore the change of A into B is *endothermic*, Q is negative and K_2 must be *greater* than K_1, that is to say, the ratio $\dfrac{C_2}{C_1}$ has a higher value at T_2 than it has at T_1. In other words, if the reaction $A \longrightarrow B$ is endothermic, the equilibrium mixture at the higher temperature T_2 will contain a larger proportion of B than at the lower temperature T_1—and conversely.

If we have determined Q experimentally, and we know the proportions of A and B at T_1, we can calculate by means of the above formula what will be the proportions at T_2. Conversely, if we determine by experiment the proportions of A and B in the equilibrium mixture at T_1 and T_2 respectively, we can calculate Q, the heat of reaction. It is assumed that Q does not change appreciably between T_1 and T_2.

IV. **69. Catalysis.** The student is doubtless already well acquainted with numerous chemical changes which are greatly influenced by the addition of a "foreign"

substance—a substance, that is, which is not included in the chemical equation representing the change. A few typical examples may be quoted.

The decomposition of potassium chlorate at a temperature a little above its melting point is very slow; the addition of a very small proportion of manganese dioxide enormously accelerates the change.

Hydrogen dioxide very slowly decomposes when its aqueous solution is warmed; the addition of a minute quantity of colloidal platinum causes a rapid decomposition, even at the ordinary temperature.

Cane sugar when heated with water undergoes, apparently, no change, but if a small quantity of dilute sulphuric acid is added it rapidly changes to a mixture of dextrose and laevulose.

Hydrogen and oxygen at the ordinary temperature do not appear to combine at all; the mixture may be kept for years without any appreciable trace of water being formed; yet, if a small quantity of spongy platinum be introduced into the mixture, combination takes place almost instantly with explosion. In all these actions the "foreign" substance is found at the end of the operation unchanged in quantity (although its physical state may in some cases be altered).

In the last two examples there appears to be no change at all until the foreign substance is added, whereas in the first two examples it is easy to demonstrate that slow change occurs without the foreign substances.

Most chemists now believe, however, that the difference is only one of degree; they consider that the oxyhydrogen mixture and the cane sugar solutions are in reality undergoing change before the foreign substance is added, but that the rate is so small that the change cannot be detected after long periods of time. [Although this is the prevailing view it is not quite universally accepted, some still being of opinion that the foreign substance can *initiate* a reaction which otherwise does not occur.]

The foreign substance which exerts this important

influence in such reactions is termed a *catalyst* or *catalyser*, and the whole change is spoken of as a *catalytic change* or *catalytic action*.

In order to restrict the use of this term to actions of a definite type it is now generally the custom to define a catalyst in the following way:

(1) A catalyst is a substance which by its presence is able to alter the rate of chemical change. [If it accelerates the rate it is called a *positive* catalyst; if it retards the rate it is called a *negative* catalyst.]

(2) A catalyst must be unaltered in composition and quantity at the end of the reaction, although it may in some cases be physically changed. This restriction does not exclude those cases in which the catalyst may actually take a chemical part in the change so long as it finally appears in its original composition and quantity.

(3) A catalyst cannot initiate a change which is incapable of taking place in absence of the catalyst.

(4) A catalyst cannot alter the final position of equilibrium in the reacting system. Examples of this have already been mentioned. Thus, the equilibrium in gaseous reactions such as $2HI \rightleftharpoons H_2 + I_2$, at a given temperature, is arrived at much more quickly if porous substances, such as spongy platinum, are present; but the final equilibrium state (i.e. the ratio between the concentrations of iodine, hydrogen and hydrogen iodide) is the same whether the porous substance is present or not.

(5) A characteristic feature of all true catalytic actions is that the amount of catalyst may be extremely small as compared with the amount of the substance undergoing chemical change. Thus, about a millionth of a milligram of colloidal platinum will cause a marked acceleration in the rate of decomposition of a considerable quantity of hydrogen dioxide.

The actual rate attained however does depend on the quantity of catalyst added; in many cases the rate is, within certain limits, proportional to the quantity of

catalyst added.   The *order* of a reaction (see Section 60)
is uninfluenced by the catalyst.

The mode of action of a catalyst is in most cases
obscure. Attempts have been made to explain all
catalytic actions as being due to a succession of chemical
changes; unstable substances are supposed to be first
formed and then decomposed.   Generally such explana-
tions are worthless, since the initial changes imagined are
themselves improbable.   But there are some catalytic
actions in which one can demonstrate the possibility of
intermediate steps; in such cases the explanation is
permissible, but it is still questionable whether much is
gained by making the assumption.

In Deacon's process for preparing chlorine, for example,
hydrogen chloride is oxidised by oxygen of the air in
presence of a catalyst consisting of some porous material
impregnated with a copper salt.   It is usually supposed
that cupric chloride is formed, that this breaks up into
cuprous chloride and chlorine, and that the cuprous
chloride is again converted to cupric chloride by hydrogen
chloride and oxygen—and so on.   But although the
changes referred to can be actually realised, it cannot
be proved that they actually do take place in Deacon's
process.   One might simply say that the porous material
and copper salt act as a "contact agent" in the same
way that spongy platinum acts; the reason why it so acts
may be a purely physical one.

The general character of catalytic actions may be
clearly represented if one considers that the rate of
chemical change is conditioned by a driving force (chemical
"affinity") and a resistance, i.e. that

$$\text{rate of change} = \frac{\text{driving force}}{\text{resistance}}.$$

A catalyst is then an agent which alters the resistance so
that, with a given driving force, the rate will be either
increased or diminished by the presence of a catalyst,
the latter being defined as "positive" or "negative"

accordingly. As a mechanical analogy, one may say that a positive catalyst behaves like oil in a rusty machine; the application of a very little oil will enable the machine to work faster.

70. *Examples.* Some examples of well-known catalytic actions will now be mentioned. Many of the changes referred to do not appear to take place at all unless the catalyst is present, others do take place slowly under the same conditions in absence of the catalyst; according to the prevailing theory, as above stated, they are really all of the latter class.

Spongy platinum catalyses the reactions:

$$2H_2 + O_2 = 2H_2O; \qquad H_2 + I_2 = 2HI;$$
$$2NO + 5H_2 = 2NH_3 + 2H_2O;$$
$$2NH_3 + 3O_2 = 2HNO_2 + 2H_2O; \qquad 2SO_2 + O_2 = 2SO_3;$$
$$2H.CH_2OH + O_2 = 2H.CHO + 2H_2O;$$
$$2H_2O_2 = 2H_2O + O_2.$$
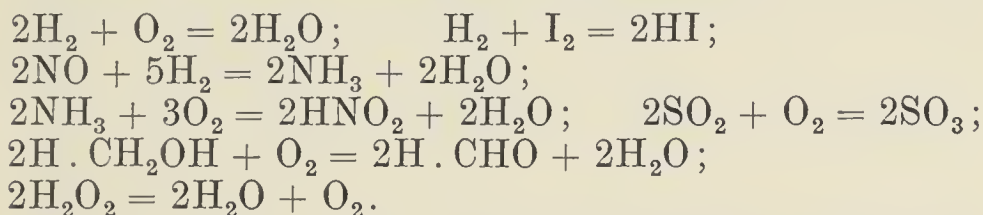
Finely divided nickel catalyses numerous reactions, including the action of hydrogen on unsaturated organic compounds and the direct resolution of many organic compounds into simpler constituents. (Sabatier and Senderen's method.)

A trace of moisture catalyses many gaseous reactions, such as:

$$2CO + O_2 = 2CO_2; \quad 2H_2 + O_2 = 2H_2O;$$
$$NH_3 + HCl = NH_4Cl; \quad NH_4Cl = NH_3 + HCl;$$
$$Hg_2Cl_2 = Hg + HgCl_2; \quad 2Na + 2HCl = 2NaCl + H_2.$$
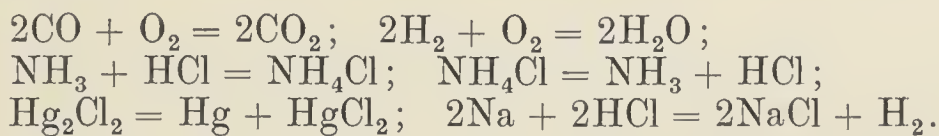
Dilute acids catalyse numerous reactions of organic substances in aqueous solution, such as the inversion of cane sugar, the hydrolysis of esters, amides, nitriles, etc., and the decomposition of diazo-compounds.

Traces of iron, in the ferrous condition, catalyse many processes of oxidation of organic substances, more especially by hydrogen dioxide.

Metallic sodium catalyses certain organic reactions, such as the condensation of isoprene to india-rubber.

Many of the above catalytic actions are of great importance in technical chemistry. Mention may also be made of the catalytic influence of a mercury salt in the oxidation of naphthalene to phthalic acid, which is used in the preparation of artificial indigo; of vanadium compounds as catalysts in the oxidation of aniline to "aniline black," and of oxides of uranium, iridium, etc. as catalysts in the synthetic production of ammonia.

71. Influence of Light. Radiations of all wavelengths, from the invisible infra-red to the invisible ultra-violet, may have marked influence on chemical changes. The fact that ordinary photographic effects are produced especially by the blue, violet and ultraviolet rays led chemists to consider that these were the most active "chemical" rays; but experience shows that this is only due to the particular substances employed (silver salts, etc.) and that all rays are active, the effect depending on the nature of the substance which absorbs the rays.

The action of light is in many respects analogous to catalytic action. Slow reactions such as the combination of hydrogen with chlorine, or with iodine, are greatly accelerated by light. But light may also behave in a manner entirely different from catalysis in that it may shift the final position of equilibrium. In the latter case light energy is absorbed and the resulting system contains more energy than the original system. Examples of the latter effect are the reduction of carbon dioxide by green plants under the influence of sunlight and the production of ozone from oxygen by ultra-violet light.

It is sometimes said that light acts as a reducing agent—but this is evidently a one-sided view. It is true that by the action of light metallic silver is produced from silver salts, ferrous salts from ferric salts, ferrocyanides from ferricyanides and so on; but it must be remembered

that an oxidising action takes place simultaneously (e.g. silver bromide gives silver and free bromine), also that the effects depend on the wave-length of the light; red rays sometimes reverse the effects produced by violet rays.

Light may also accelerate allotropic change, such as the conversion of ordinary yellow phosphorus to red phosphorus, and may bring about polymerisation, e.g. the conversion of anthracene, $C_{14}H_{10}$, into dianthracene, $C_{28}H_{20}$; the latter change is reversed in the dark.

82. *Photographic processes.* When light acts upon silver chloride, a dark coloured product is obtained which has been the subject of much discussion. Some regard it as metallic silver in a highly dispersed state; others consider it to be silver subchloride or oxychloride. In any case the change may be looked upon essentially as $AgCl \rightleftarrows Ag + Cl$, and, this being reversible, it is evident that the presence of a substance capable of combining or reacting with the chlorine will have the effect of shifting the equilibrium in the forward direction (law of mass action). This explains the action of "sensitisers" in photographic papers or plates; the silver halide is mixed with such substances as gelatine or albumen and these remove the halogen as fast as it is formed.

When silver bromide is employed, the effect of a small exposure to light is quite invisible to the eye; if however a reducing agent, of a certain type, is added, the effect rapidly becomes apparent, black silver being deposited where the light has acted (photographic development). The exact nature of this process has been explained in different ways and is perhaps not entirely understood. It may be supposed that the action of the light produces a minute invisible deposit of silver in the film; when this is immersed in a solution of the reducing agent, silver salt goes into solution and is reduced to metallic silver, which remains as a supersaturated solution. The minute particles of silver, which resulted from the

action of light, then act as nuclei upon which more silver is deposited.

In order to *fix* the photographic image it is, of course, necessary to remove all the unaltered silver bromide or chloride. With this object, the print, or the negative, is immersed in a fairly strong solution of sodium thiosulphate. The unaltered silver bromide or chloride dissolves, forming the salt $Na(AgS_2O_3)$ which is easily soluble, and the reduced silver remains unaffected. In obtaining photographic prints, many other processes are used. For instance, ferric oxalate on exposure to light is reduced to ferrous oxalate and if this is acted upon by a solution of a platinous salt, black metallic platinum results (Platinotype process). Or the ferric oxalate print after exposure may be acted upon by potassium ferricyanide, when dark (Turnbull's) blue is produced where the light has acted (Blue printing). Blue prints may also be obtained by using potassium ferricyanide, which on exposure to light becomes ferrocyanide, and developing the print with a ferric salt.

When gelatine is mixed with a small quantity of potassium dichromate and exposed to light, a compound is formed which is very sparingly soluble in warm water. In the "carbon process," a plate or paper is coated with gelatine which is coloured with a suitable pigment and is then "sensitised" by dipping it into potassium dichromate solution. On exposure under a negative the parts acted upon by light become insoluble, or nearly so, and on washing with warm water the parts unacted upon are dissolved away.

CHAPTER VI

THERMO-CHEMISTRY

73. All chemical changes are accompanied by energy
changes; if the change is a spontaneous one, the result
is always a loss of "free" or "available" energy, that is
to say, the resulting system possesses less capability of
doing work than the initial system. This change of
energy may be manifested in various ways, the most
common of which are evolution of heat and performance
of external work. When, for example, 65 grams of zinc
are dissolved in dilute sulphuric acid, 34,200 calories are
evolved and, at the same time, work is done by the
resulting hydrogen in overcoming the atmospheric pres-
sure. [This work is $2T$ calories, where T is the absolute
temperature at which the operation takes place. See
Section 6 a.]

In most chemical changes the thermal change is by
far the most obvious and the external work, even in the
case of gases, is small in comparison. This thermal
change is in most cases positive, i.e. heat is evolved, if
the action takes place spontaneously. Berthelot supposed
that all spontaneous chemical changes must necessarily
be exothermic and that, if a reaction can proceed in
various ways, it will always proceed spontaneously in
that direction in which most heat is evolved. This
could only be so if the evolution of heat were a measure
of the free energy of the system. We see however
that this is not necessarily the case, since some reactions
occur spontaneously with absorption of heat and also

since we can in many cases prove that external work is done. It can be shown theoretically that Berthelot's rule would be true at absolute zero; it holds true also in cases in which the available energy does not change with temperature. (Compare Section 87.)

At absolute zero, all spontaneous chemical changes would be exothermic; all the available energy would appear as heat. The nearer the temperature is to absolute zero the more nearly does Berthelot's rule hold, and the reason why the rule is so often approximately true at the ordinary temperature is that this temperature is not so far removed from absolute zero.

The term *chemical affinity* has been employed in numerous different ways; generally, it implies "tendency to combine or react." In order to give the term a precise meaning it is now the custom to define it as the "driving force" of a chemical change and this driving force is measured by the *maximum work* which the change can do, i.e. by the *free energy* of the system. According to this view, chemical affinity is the "intensity factor" of chemical energy, just as temperature is the intensity factor of heat energy and difference of potential that of electric energy. A spontaneous chemical change takes place in the direction in which the free energy diminishes; most often at low temperatures this loss of free energy is manifested by evolution of heat and the heat evolved is taken as a rough measure of the free energy of the system.

It will be evident therefore that the determination of the thermal changes which accompany chemical reactions is of considerable importance since it gives information with regard to the energy changes. If we know the thermal values it is often possible to predict, with a fair amount of certainty, whether a given change will take place spontaneously or not.

By the *heat of reaction* is meant the number of units of heat which are evolved or absorbed when the reaction takes place completely as indicated by the chemical equation, the quantities reacting being represented by

the formula weights. Thus when we say that the heat
of combustion of charcoal is 96,960, we mean that 12 grams
of carbon, in the form of charcoal, when completely
burnt in oxygen, gives 96,960 gram calories. The result
is usually expressed as

$$C + O_2 = CO_2 + 96960,$$
$$\text{solid}\quad \text{gas}\quad \text{gas}$$

or as $$C, O_2 = + 96960.$$
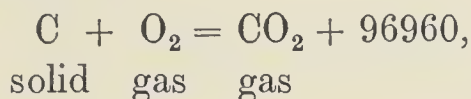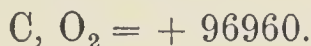
[Note that in chemistry it is the custom to regard
heat *evolved* as positive and heat *absorbed* as negative.
In physics the opposite signs are generally used.]

Similarly, the *heat of formation* of a compound means
the number of units of heat evolved or absorbed in the
formation of one formula-weight of the compound from
its constituents. Thus, the heat of formation of carbon
dioxide (from charcoal) is $+ 96960$ and the heat of for-
mation of carbon disulphide is $- 19610$. We say that
carbon dioxide is an exothermic compound and carbon
disulphide endothermic.

The heat evolved in the formation of a compound is,
of course, equal, and of opposite sign, to the heat absorbed
in its decomposition, provided that the initial and final
states are the same in the two cases; e.g. the heat of
decomposition of carbon dioxide would be $- 96960$ if the
result of the decomposition was solid charcoal and oxygen
gas.

Another fairly obvious rule has to be remembered in
working out calculations in thermal chemistry; it is
called the *law of constant heat summation*. It states that
the total heat of a reaction depends only on the initial and
final states and is independent of any intermediate steps
by which the reaction may be brought about. Thus, if we
burn 12 grams of charcoal to carbon dioxide we obtain
96,960 calories. We might however first obtain carbon
monoxide from 12 grams of charcoal; this would give
29,000 calories and when the carbon monoxide was

further burnt to carbon dioxide, we should obtain 67,960 calories.

74. The expression *calorific power* is sometimes used in technical work; one speaks, for example, of the calorific power of a fuel. This is the number of units of heat evolved in complete combustion of *unit mass* of the substance. [In chemistry we define *heat of combustion* of a substance as the number of units of heat evolved in the complete combustion of *one formula-weight* of it.]

The term *calorific intensity* is similarly used to denote the maximum *temperature* which could be produced by combustion of the substance under stated conditions, i.e. we speak of the calorific intensity of the substance when burnt in oxygen or in air. If we know the calorific power of a substance we can calculate its calorific intensity, provided we know the specific heats of the products, and if we assume that all the heat is retained in these products.

Thus the calorific power of charcoal is 8080 and, on combustion, one gram of charcoal produces (approximately) $\frac{44}{12}$ grams of carbon dioxide. If we take 0·2164 as the specific heat of carbon dioxide, we have (from the relation $Q = wst$)

$$8080 = 3·66 \times 0·2164 \times t.$$

This gives the calorific intensity t as about 10,000°, which is, of course, absurdly high. The reason is that the specific heat varies considerably with temperature and also that the heat is not in reality all retained by the product; much escapes by conduction, radiation, etc.

75. *Determination of the heat of reaction.* The heat of reaction, heat of formation, etc. may be determined either directly or indirectly. For the direct determination, weighed quantities of the substances are allowed to react in a vessel surrounded by a known quantity of water and the rise in temperature of the water is noted. This direct method can, of course, only be used for cases in which the reaction takes place rapidly and completely.

For indirect determination use is made of the law of constant heat summation (see above). If, for example, we wish to determine the heat of formation of methane, it is evident that the direct method is impossible since carbon and hydrogen do not combine, except very incompletely and at very high temperatures. But if we

burn methane to carbon dioxide and water and measure the heat evolved, and if we know the heats of combustion of carbon and of hydrogen, we can calculate the heat of formation of methane. For, according to the law referred to, the total quantity of heat evolved on burning 12 grams of carbon and 4 grams of hydrogen to carbon dioxide and water will be just the same whether we do so directly, or whether we first cause the carbon and hydrogen to combine to form methane and then burn this methane to carbon dioxide and water. The fact that we cannot combine the carbon and hydrogen *practically* does not matter. The relation may be expressed by saying that the heat of formation of a compound is equal to the heat of combustion of its free constituents *minus* the heat of combustion of the compound itself. Thus, for methane we have

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 211930,$$
$$2H_2 + O_2 = 2H_2O + 136420,$$

and $$C + O_2 = CO_2 + 96960.$$
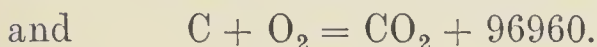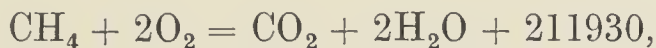
Therefore the heat of formation of methane is

$$136420 + 96960 - 211930 = + 21450.$$

For acetylene, the heat of combustion is 310450. But the heat developed by burning 24 grams of carbon and 2 grams of hydrogen is $193920 + 68210 = 262130$. More heat then is obtained by burning the compound than by burning its free constituents. The heat of formation of acetylene is therefore $- 48320$, i.e. acetylene is an endothermic compound.

As another example of this indirect method of calculating the heats of formation of compounds the following may be mentioned. The heat of formation of hypochlorous acid of course cannot be directly determined. But we know the heat evolved when one gram molecule of chlorine acts on caustic potash solution to produce potassium hypochlorite, potassium chloride and water;

call this Q.   Now we may imagine that the first change is

$$Cl_2 + H_2O = HClO + HCl,$$

and that these acids are then neutralised by the caustic potash; the total heat evolved in these changes would be the same as the heat evolved when chlorine and caustic potash are converted directly into potassium chloride, hypochlorite and water, except that one molecule of water would be decomposed when the change took place in stages.

Q will therefore be equal to the heat of formation of hypochlorous acid + the heat of formation of hydrochloric acid + the heats of neutralisation of these acids − the heat of formation of water.   All the other values having already been determined, we can calculate the heat of formation of hypochlorous acid.

An entirely different method for calculating heats of formation, heats of reaction, etc. has already been indicated in Section 68.   We determine the equilibrium constants K_1 and K_2 at two different temperatures T_1 and T_2 (absolute) and calculate the heat of reaction Q from the formula

$$\log_e K_1 - \log_e K_2 = \frac{Q}{2}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

In this calculation it is assumed that Q remains constant between the two temperatures, which is usually approximately true if T_1 and T_2 are not far apart.

CHAPTER VII

ELECTRO-CHEMISTRY

76. Electrolytic dissociation. Salts, acids and bases, when dissolved in water, yield solutions which conduct the electric current, the passage of the current being accompanied by definite chemical changes at the electrodes. These substances are called *electrolytes* as distinguished from other substances which give non-conducting solutions. Most organic compounds, such as sugars, ethers, alcohol, urea, etc., belong to the latter class.

Electrolytes have also other distinguishing properties; for example, their solutions in water (and in certain other solvents, see Section 41 *a*) have abnormally high osmotic pressures. They are, as a class, more chemically reactive than non-electrolytes, and those which are the most reactive are usually the ones whose solutions are the best conductors and which show the greatest deviation from the normal osmotic pressure. Further, the physical and chemical properties of solutions of electrolytes are usually of an additive character, i.e. they seem to be made up of two factors, one depending on the metallic or positive part and the other on the acidic or negative part.

These peculiar properties of electrolytes have been accounted for in a variety of different ways, but the only theory which gives a comprehensive and quantitative explanation of nearly all the facts is that of electrolytic dissociation.

This theory assumes that the electrolyte when dissolved in water becomes split up to some extent into constituent parts or *ions*, which are charged with large quantities of electricity. The metallic or positive part of the electrolyte carries a positive charge and the negative or acidic part a negative charge, the essential condition being that these positive and negative charges shall be equal and opposite. The ions are therefore the separated atoms or groups of which the electrolyte is constituted, carrying enormous electric charges and able to move about independently of one another. The properties of these charged atoms are, of course, entirely different from those of their neutral molecules; the sodium ion, for example, has no resemblance to metallic sodium as we know it. This splitting up of the electrolyte into ions is a reversible process depending on the dilution, on the nature of the electrolyte and solvent and, to some extent, on the temperature. It differs essentially from ordinary dissociation, such as that of ammonium chloride or calcium carbonate, in that the products of the dissociation are electrically charged. For this reason the phenomenon is distinguished by the name "ionisation" or "electrolytic dissociation."

It must be distinctly understood that this theory is used only as a working hypothesis; there are still many who do not believe that ionisation does occur when an electrolyte merely dissolves in water; it is not necessary however to believe or disbelieve it without further evidence, and meanwhile, if used as a provisional working hypothesis, it serves to explain, in a clear and simple way, an enormous number of facts. It is the only theory, moreover, by which these facts can be dealt with in a quantitative way. It is true that this quantitative treatment gives satisfactory results only in the case of *dilute* solutions; but the same may be said of the simple gas laws; in order to account quantitatively for the behaviour of strong solutions or of compressed gases, the simpler theories have to be modified or amplified.

It can be shown by electrolytic experiments that each univalent ion carries the same electric charge— namely 96,540 coulombs (see page 175), which may be regarded as the unit ionic charge—and that an ion which is n-valent carries n times this charge.   In representing the process of ionisation by a chemical equation, it is usual to denote the number of unit ionic charges by a dot or dash, or by the symbol $+$ or $-$, according as the charge is positive or negative.   Thus the ionisation of sodium chloride is represented as $NaCl \rightleftarrows \dot{Na} + Cl'$, or as $NaCl \rightleftarrows \overset{+}{Na} + \overset{-}{Cl}$.

The *degree of ionisation* of an electrolyte is the fraction of it which is ionised; thus if under given conditions of dilution etc. it is found that 50 per cent. of the original molecules become ionised we say that the degree of ionisation, under these conditions, is 0·5 and so on.

The degree of ionisation increases with dilution in a manner which will be indicated below.   Most salts, especially those of a monobasic acid with a monacid base, like KCl, are strongly ionised even at a moderate dilution.   Thus potassium chloride is about 80 per cent. ionised in a $\frac{1}{4}$ normal solution at ordinary temperature. The degree of ionisation of acids and bases varies very greatly; the strong acids and bases like HCl and NaOH are largely ionised at moderate dilution, whereas weak acids and bases like HCN and NH_4OH are very slightly ionised.   On dilution, the degree of ionisation of most salts and of strong acids and bases increases up to a limit beyond which it becomes practically constant, corre- sponding to complete ionisation; but in case of weak acids and bases it is practically impossible to reach this dilution.   Theoretically, at infinite dilution, all elec- trolytes would be completely ionised.   Polybasic acids ionise in stages: H_2SO_4 ionises first as $\dot{H} + (HSO_4)'$ and on greater dilution as $\dot{H} + \dot{H} + (SO_4)''$ and ortho- phosphoric acid as $\dot{H} + (H_2PO_4)'$, $2\dot{H} + (HPO_4)''$ and $3\dot{H} + (PO_4)'''$.

The leading properties of dilute solutions of electrolytes are, according to this theory, the properties of the separate ions. Thus, all cupric salts, in dilute solution, owe their blue colour to the cupric ion $\overset{..}{C}u$, and all solutions of chlorides give a precipitate with silver nitrate owing to the chlorine ion Cl'; these properties are independent of the nature of the acidic and the basic ion respectively. Acids, in solution, owe their "acidic" properties to hydrogen ions, whilst the basic or alkaline properties of metallic hydroxides are due to hydroxyl ions.

77. *Application of the law of mass action.* The general laws referred to in previous sections, which govern chemical changes, such as the law of mass action and the principle of Le Chatelier, may, of course, be applied in considering the reversible process of ionisation. In order to illustrate the application of the law of mass action, consider, for the sake of simplicity, an electrolyte MX consisting of two univalent ions. Suppose that one mol of it (one molecular weight of it in grams) is dissolved in V litres of water and that m is the degree of ionisation which it undergoes. The solution will now contain $1 - m$ moles of the non-ionised substance and m moles of *each* of its ions, since the ions are produced in equivalent proportion. According to the law of mass action therefore, when equilibrium is attained in the reversible system, $MX \rightleftarrows \overset{.}{M} + X'$, we shall have

$$\frac{1 - m}{V} K = \frac{m}{V} \cdot \frac{m}{V}, \text{ or } K = \frac{m^2}{(1 - m) V}.$$

[K is the equilibrium constant, called in this case the *dissociation constant* or *ionisation constant*. It depends on the nature of the electrolyte and the temperature.] This relation is, for shortness, often written $KC = ab$, where C, a and b are the *concentrations* of the non-ionised part and the two ions respectively. In the particular example here given, $a = b$. This relation shows us at once how the degreee of ionisation alters with dilution. It is known as Ostwald's *dilution law*. [If

the degree of ionisation is very small, as in the case of very weak acids, it is evident that $1 - m$ is very nearly 1; in this case we shall have, nearly, $K = \dfrac{m^2}{V}$ or $K = \dfrac{m}{\sqrt{V}}$; i.e. the degree of ionisation varies nearly as the square root of the volume.]

This dilution law holds remarkably well in the case of weak electrolytes; with strong electrolytes very considerable deviations occur. These deviations are not completely understood; they may possibly be due to hydration or to the formation of complex ions.

A brief indication will now be given of the application of the ionic dissociation hypothesis in explaining the behaviour of electrolytes in aqueous solution.

78. *Electrolytic conduction.* The theory of ionisation affords a strikingly simple and quantitative means of explaining the phenomena of electrolysis. The older theories, while accounting qualitatively for many of the facts, were found wanting when tested in a quantitative way. It used to be thought that the molecules of the electrolyte were "torn asunder" at the electrodes by the electric force. If this were the case one would expect that no electrolysis should begin until a certain minimum electromotive force was reached. It can be shown however that if the effect of polarisation is eliminated (see Section 92) electrolysis can take place even with the smallest electromotive force and that the current is proportional to the electromotive force for all values of the latter. Further, it was sometimes supposed that the positive and negative constituents obtained at the electrodes arose from the same molecule, i.e. that on electrolysis of the molecule AB, its positive constituent A appeared at one electrode and its negative constituent B at the other. This cannot be the case since the products appear at the electrodes as soon as the current begins, even if the electrodes are far apart, and it will be shown later that the actual rates at which the parts travel through the

liquid are very slow. In order to account for this, it was suggested that the first effect of the electromotive force is to set all the molecules between the electrodes in a line, with their positive parts facing towards one electrode and their negative parts towards the other. The molecules next to the electrodes were then split up by the electric force, one constituent being liberated and the other working its way through the liquid by changing partners with the intermediate molecules (Grotthuss's hypothesis).

In this case it would appear that the rate at which electricity is conveyed through the liquid should depend upon the frequency with which the molecules collide with one another. But it can be shown, on the kinetic theory, that this frequency depends on the square of the concentration of the molecules; the conductivity of the liquid should depend directly on the frequency of collisions and also on the concentration; i.e. it should vary, approximately at any rate, as the cube of the concentration, whereas experiment proves that in dilute solutions it varies as the first power of the concentration.

To get over these difficulties Clausius suggested that a certain small proportion of the electrolyte exists in solution in the dissociated state, and that on applying electromotive force these dissociated parts are directed towards the electrodes and there discharged. As these dissociated parts are removed from the sphere of action, more molecules dissociate so as to restore the original state of equilibrium and these new parts are again removed, and so on. According to this theory the electromotive force is merely *directive*. It does no breaking up or "tearing asunder" of the molecules; the only work it does is that necessary to drive the ions through the liquid against the frictional resistance.

This theory was modified, extended and put into a quantitative form by Arrhenius, and he showed that, in terms of it, we can satisfactorily explain not only the phenomena of electrolytic conduction, but also the

abnormally high osmotic pressures given by electrolytes in aqueous solution.

79. *Osmotic pressure of electrolytes.* It has already been mentioned that electrolytes in aqueous solution give osmotic pressures which are abnormally high; this is true, of course, whether the osmotic pressure is determined directly, or indirectly, by means of phenomena such as the lowering of the freezing point or rise of boiling point. Thus when one molecular weight of a non-electrolyte, such as urea, is dissolved in a given volume of water, we can calculate the osmotic pressure, lowering of freezing point, etc. by means of the general laws referred to in previous sections. We know that the gas laws will be obeyed if for "gas pressure" we substitute "osmotic pressure" so that one mol, or 60 grams, of urea in 22·4 litres of water at 0° will produce an osmotic pressure of 760 mm. But in the case of electrolytes the pressures obtained are always too large, the deviation being greater as the solution becomes weaker up to a certain limit. If we dissolve 1 mol or 58·5 grams of common salt in 22·4 litres of water at 0° the osmotic pressure will be considerably greater than 760 mm., and in a solution about $\frac{1}{8}$ normal the value will be about 2×760. In fact, nearly all binary salts consisting of a univalent metal and univalent acid radicle give, in dilute solution, osmotic pressures which are about double the calculated value; salts, like barium chloride, of a bivalent metal and univalent acid radicle give about three times the normal value. These deviations were expressed numerically by van't Hoff as the ratio of the observed to the calculated value and this ratio was denoted by the symbol i. This symbol i then denotes the number by which the calculated value has to be multiplied in order to give the observed value. For non-electrolytes $i =$ about 1; for very dilute solutions of NaCl it is about 2, and for very dilute solutions of $BaCl_2$ it is about 3.

These deviations are, of course, easily accounted for

in terms of the theory of electrolytic dissociation if we assume that each ion produced can behave, as regards osmotic pressure, as if it were a molecule; one molecule of sodium chloride, for example, when dissolved in a sufficiently large quantity of water, gives rise to two parts, each of which gives rise to the same osmotic pressure as one molecule of a non-electrolyte gives under the same conditions; one molecule of barium chloride yields three such parts, and so on. If the dilution is such that only part of the electrolyte is ionised, the observed osmotic pressure will be due both to molecules and ions. Thus, if one molecule of the electrolyte can yield two ions and if it is ionised to the extent m, i.e. if m is the degree of ionisation, we shall have in solution $2m$ as ions and $1 - m$ in the non-ionised state. The osmotic pressure produced will therefore be $1 - m + 2m$ times as great as it should be or, in terms of the symbol used above, we have
$$i = (1 - m) + 2m.$$
Generally, if one molecule can split into n ions and m is the degree of ionisation,
$$i = 1 - m + nm \text{ or } m = \frac{i - 1}{n - 1}.$$

If therefore we determine i from the osmotic pressure or freezing point, boiling point, etc. we can calculate the degree of ionisation (compare Section 76).

For example, a normal solution of sodium chloride freezes at about $- 3.26°$, and according to Raoult's law it should, if undissociated, freeze at $- 1.85°$; hence
$$i = \frac{3.26}{1.85} = 1.76,$$
and, since NaCl gives 2 ions,
$$m = \frac{1.76 - 1}{2 - 1} = 0.76.$$

The ionic dissociation hypothesis thus offers a simple quantitative explanation of "abnormal" osmotic pressures just as the theory of ordinary dissociation does

of "abnormal" vapour densities. Many attempts have been made to explain the abnormal osmotic pressures of electrolytes without making use of the ionic dissociation hypothesis; most of the explanations proposed are, however, merely qualitative and often introduce fresh difficulties. Thus, it has been suggested that the dissolved electrolyte combines with some of the water to produce a chemical compound, or hydrate; in this way the "effective" quantity of the water is diminished and therefore the solution is more concentrated, i.e. the ratio of pure solvent to dissolved substance is less than it would be if no chemical combination occurred. But it would require an enormous number of molecules of water to unite with one molecule of the electrolyte in order to give the observed result; in a $\frac{1}{8}$ normal solution of sodium chloride, for example, nearly half of the water would have to be combined with the salt.

Again, it has been suggested that the high values given by electrolytes are the correct ones and that the lower values given by non-electrolytes are "abnormal," due to these substances being associated; this is ruled out by the fact that the normal value can be calculated from the theory of dilute solutions and it agrees with the results given by non-electrolytes.

As regards salts, it was suggested that the high values might be due to hydrolysis, i.e. the action of water on the salt might yield acid and base; one molecule of $NaCl$ would give rise to one molecule of HCl and one of $NaOH$, so we should obtain two molecules in solution in place of one. Similarly, $BaCl_2$ would give $Ba(OH)_2$ and $2HCl$; three molecules instead of one. But such an explanation could not be applied to HCl or to $NaOH$ themselves, both of which give results about as high as $NaCl$.

80. *Solubility of electrolytes.* The solubility of a solid, as previously indicated, is the maximum concentration of the solution which is in contact with the solid; the molecules of the substance in the solid state are then

in equilibrium with molecules of the same substance in solution. In case of electrolytes, however, a certain number of the molecules in solution undergo ionisation; hence more solid will have to go into solution to replace those ionised molecules in order that equilibrium may be maintained. We have then two different conditions of equilibrium to consider, first that between the solid and its un-ionised molecules in solution, and, secondly, that between the molecules in solution and the ions.

As regards the first, we know, from the laws of solubility, that C, the maximum concentration of the un-ionised molecules, must, at a given temperature, be constant. As regards the second, we know from the law of mass action that $KC = ab$, where C is the concentration of the un-ionised part and a and b are the concentrations of the ions respectively. But since C is constant, $a \times b$ must also be constant. We see therefore that at a given temperature if the solid salt is present and is in equilibrium with the saturated solution, the product of the concentrations of the ions must be constant. This product is called the *solubility product*. When this value is exceeded the solution becomes supersaturated and precipitation occurs.

In terms of this theory we can explain a large number of the facts met with in analytical chemistry. It is well known, for example, that a nearly saturated solution of sodium chloride is precipitated if hydrochloric acid gas is passed into it. In the nearly saturated solution, we have both $\dot{N}a$ and Cl' ions, but the product of their concentrations does not reach the value of the solubility product. If however we add HCl, which in solution is strongly ionised, we increase the total concentration of the Cl' ions; the concentration of the $\dot{N}a$ ions is thereby diminished and that of the non-ionised $NaCl$ is increased, in order that equilibrium may be maintained; i.e. since $KC = ab$, increase of b will have the effect of diminishing a and increasing C. When C exceeds the saturation value, the solution will become supersaturated and, under

usual conditions, precipitation will begin. In a similar way we may explain the fact that in order to obtain "complete" precipitation, an excess of the reagent must usually be added.

81. *Complex ions.* In some cases addition of excess of the precipitating reagent causes the original precipitate to dissolve. This, as a rule, is due to the formation of a *complex ion* which contains one of the ions of the original precipitate as a constituent. Thus, for example, when caustic soda is added to zinc sulphate in dilute solution we have originally present the ions Na, $\ddot{\mathrm{Zn}}$, (OH)′ and $(SO_4)''$; since the solubility product of zinc hydroxide happens to be small, there will be, even in dilute solution, sufficient concentration of $\ddot{\mathrm{Zn}}$ and (OH)′ to reach the value [in this case the concentration of $\ddot{\mathrm{Zn}}$ multiplied by the *square* of the concentration of (OH)′].

When more caustic soda is added some of the zinc ions become converted into the acidic ion $(ZnO_2)''$; the concentration of the simple $\ddot{\mathrm{Zn}}$ ions is thereby reduced and the solubility product of zinc hydroxide is no longer reached. Hence the solid zinc hydroxide will dissolve again.

Similarly, we can explain the solubility of silver chloride in ammonia, the silver ions going to form the complex cation $(AgNH_3)$, or of silver chloride in sodium thiosulphate, in which case the complex anion (AgS_2O_3) is produced. The formation of complex ions also explains why the usual qualitative tests for a metal or acid radicle may, in certain cases, entirely fail to detect the substance, although one knows it is there. Potassium ferrocyanide gives none of the tests for iron, because the metal is present in solution as the complex anion $(FeC_2N_2)^{iv}$; the tests for iron in solution are tests for the simple $\ddot{\mathrm{Fe}}$ or $\dddot{\mathrm{Fe}}$ ions, the complex gives entirely different reactions.

Such complex ions exist in solution in equilibrium

with the simple ions from which they were derived; but the proportion of simple to complex varies greatly in different cases. In potassium ferrocyanide there probably may be $\overset{..}{Fe}$ and $(CN)'$ ions, but the amount is too small to be recognised. In the reaction $2KCN + Cd(CN)_2 \rightleftarrows K_2[Cd(CN)_4]$, however, we must assume the existence of both simple and complex ions since hydrogen sulphide precipitates CdS, whereas alkalis do not precipitate $Cd(OH)_2$; i.e. the concentration of $\overset{.}{Cd}$ ions is sufficient to give, with the S'' ions, the solubility product of CdS but is not, with the $(OH)'$, sufficient to reach that of $Cd(OH)_2$. In case of the corresponding copper compound the concentration of $\overset{..}{Cu}$ ions is insufficient for the precipitation of copper sulphide. Based upon this fact is one of the methods of separating copper from cadmium.

82. *Neutralisation.* According to the hypothesis of ionic dissociation, acids in solution owe their "acidity" to hydrogen ions, and alkalis their alkalinity to hydroxyl ions. Hence in a perfectly neutral liquid, either these ions are absent or else they are present in equivalent quantities. It can be shown in various ways that pure water contains both $\overset{.}{H}$ and $(OH)'$ ions but in extremely minute quantities—about a ten-millionth gram ion per litre at 25°. Here, of course, the two ions are present in exactly equivalent quantities if water ionises as $H_2O \rightleftarrows \overset{.}{H} + (OH)'$. If a solution contains any excess of $\overset{.}{H}$ over $(OH)'$ it will be acid and if the $(OH)'$ exceeds the $\overset{.}{H}$ it will be alkaline. The "indicators" we employ in analytical chemistry may be regarded as tests for this excess; they vary however very much in their sensitiveness. Thus the acidity of a solution of carbonic acid is easily demonstrated by phenolphthalein, but not by methyl orange.

The indicators usually employed have themselves the character of weak acids or weak bases and the colour changes which they experience may be explained by supposing that one of the ions has a different colour from

that of the non-ionised molecule. Thus, if we regard phenolphthalein as an acid HX we may suppose that the un-ionised molecule is colourless and the acid radicle X′ is pink. With methyl orange, regarded as an acid, HX is pink and X′ is yellow, and with litmus HX is red and X′ is blue. In the aqueous solution of the indicator we have the equilibrium

$$HX \rightleftarrows \dot{H} + X′,$$

and, on adding an acid, the effect is that the concentration of $\dot{H}$ is increased and that of X′ diminished with formation of more HX. Since the indicator is a very weak acid, a very little additional acid is sufficient, practically, to "suppress" X′ altogether beyond visible recognition. The addition of a base, on the other hand, supplies (OH)′ ions which react with the $\dot{H}$ ions of the indicator acid to produce water; equilibrium is thus disturbed and further ionisation of HX results. Consequently more X′ is produced and its colour becomes apparent.

The colour changes of indicators may be explained, without reference to the ionic hypothesis, by the fact that the substances employed are known to undergo a change of constitution under the influence of acids and alkalis. This fact, however, does not at all interfere with the ionic explanation.

The neutralisation of an acid by a base is represented by the ordinary chemical equation as a replacement of hydrogen in the acid by the metal of the base, water being formed at the same time,

$$HX + MOH = MX + HOH.$$

In terms of the ionisation hypothesis, the process is regarded differently, since both the acid and base are more or less ionised to start with, and so is the resulting salt. In the case of strong acids, bases, and most salts, in dilute aqueous solution, this ionisation is nearly complete and the process of neutralisation may then be represented with sufficient accuracy as

$$\dot{H} + X′ + \dot{M} + (OH)′ = \dot{M} + X′ + HOH,$$
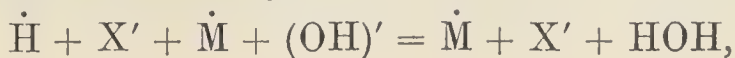
that is to say, the only change which has occurred consists in the combination of $\dot{H}$ and $(OH)'$ to form water, the $\dot{M}$ and X' ions taking, practically, no part.

This theory of the process offers a remarkably simple explanation of the well-established fact that the heats of neutralisation of all the strongest acids with the strongest bases are about the same, e.g. HCl, HNO_3 or HBr when neutralised with either NaOH, KOK or LiOH all give about 13,700 gram calories per gram molecule. On this view, then, the heat of neutralisation of strong acids and bases in dilute solution is the heat evolved by combination of $\dot{H}$ with $(OH)'$, i.e. the heat of formation of water from its ions. With weaker acids or bases, the heat of neutralisation differs considerably from 13,700. This is explained by saying that the acid or base is not completely ionised to start with and its complete ionisation, which must precede complete neutralisation, is attended with either absorption or evolution of heat. Thus, the heat of neutralisation of hydrofluoric acid by a strong base is greater than 13,700, whereas that of acetic acid is less than 13,700. Therefore it is concluded that in the ionisation of the former heat is evolved and in that of the latter heat is absorbed.

The *heats of ionisation* of electrolytes have been determined in other ways and it is shown that the values may be either positive or negative.

83. *Hydrolysis of salts.* Salts of weak acids or weak bases when dissolved in water undergo, to some extent, the change which may be represented as

$$\text{salt} + \text{water} \rightleftarrows \text{acid} + \text{base};$$

this is known as *hydrolysis* of the salt. According to the older views, this change consists in the double decomposition of salt and water, the metal combining with hydroxyl and the acid radicle combining with hydrogen. In terms of the ionisation hypothesis the change is regarded quite differently. Suppose, for example, that

we start with a salt MX derived from a strong* base MOH and a weak acid HX. According to the ionic hypothesis, the salt in solution ionises considerably to $\dot{M} + X'$, the base considerably to M + OH, the acid very slightly to $\dot{H} + X'$, and the water very slightly to $\dot{H}$ and (OH'). If the acid is very weak and the base very strong, the final products obtained by dissolving the salt in water will therefore be, for the most part, the acid HX and the ions $\dot{M}$ and (OH'),

$$\dot{M} + X' + \dot{H} + (OH)' = \dot{M} + (OH)' + HX,$$
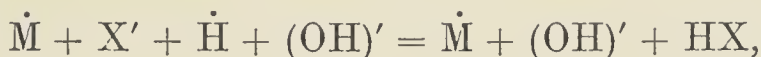
the essential change being the combination of the X' ions from the acid with the hydrogen ions from the water. As a result, the solution will contain a considerable concentration of free $(OH)'$ and will therefore react alkaline. Conversely, if the base is very weak and the acid very strong, we shall have, for the most part,

$$\dot{M} + X' + \dot{H} + (OH)' = \dot{H} + X' + MOH,$$
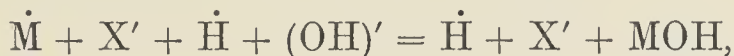
the principal change consisting in the combination of $\dot{M}$ with $(OH)'$; as a result, the solution will contain free $\dot{H}$ ions in considerable concentration and will therefore react acid. If both the acid and base from which the salt is derived are very weak the change will be, for the most part,

$$\dot{M} + X' + \dot{H} + (OH)' = HX + MOH.$$

In this case, if both the acid and base are equally weak, the solution will be neutral, since there will be no excess of $\dot{H}$ or $(OH)'$.

84. Hydrolysis of a salt then, according to this view, is due to the combination of one of the ions of water with one of the ions of the salt, or, in the case where both acid and base are very weak, both ions of water combine respectively with the ions of the salt. It is sometimes a puzzle to students how, according to this view,

* See Section 85.

a salt can become largely hydrolysed, since we know that the degree of ionisation of water is so minute. It must be remembered however that in the solution the equilibrium in several simultaneous reversible reactions has to be satisfied; that between the acid (or base) and its ions, that between water and its ions, and that between the salt and its ions. In each case the equilibrium is regulated by the law of mass action and the final result will therefore depend on the concentrations of the various substances and on the dissociation constants. Thus for a salt MX, derived from a very weak acid and a strong base, we have

$$MX \rightleftarrows \dot{M} + X'; \quad HOH \rightleftarrows \dot{H} + (OH)' \text{ and } HX \rightleftarrows \dot{H} + X',$$

each being regulated by the relation $KC = ab$, where K is the dissociation constant of the substance in question. In the first K is large and in the two latter very small. Hence we have a large concentration of $\dot{M}$ and X' and in order to satisfy the relations between $\dot{H}$ and X' a considerable quantity of $\dot{H}$ must be used up. But this can only come from the ionised water and hence more water must ionise in order to maintain the necessary relations between $\dot{H}$ and X', $\dot{H}$ and $(OH)'$ and $\dot{M}$ and $(OH)'$. If, for simplicity, we regard the salt and base as completely ionised, it is evident that the degree of hydrolysis will depend on the relative values of the dissociation constants of the acid and of water.

The degree of hydrolysis becomes greater as the *temperature* is higher. This can be predicted from Le Chatelier's principle (Section 67) since heat is evolved when an acid neutralises a base; hence when a salt is "unneutralised," heat will be absorbed.

As regards the influence of *dilution* on hydrolysis, it is found that in the case of salts derived from weak acids and strong bases, or weak bases and strong acids, the degree of hydrolysis increases with dilution. If, however, the acid and base are both very weak, the degree of hydrolysis is independent of dilution. In terms of the ionic hypothesis it can easily be shown that these results are in accordance with the law of mass action.

85. *Strength of acids and bases.* The general properties of acids which are considered to be characteristic of them as a class—such as sour taste, powers of neutralising alkalis, decomposing carbonates, dissolving metals etc.—are evidently more pronounced in some acids than

in others.   In sulphuric, nitric and hydrochloric acids,
for example, these properties are very strongly marked,
whereas in boric, carbonic and hydrocyanic acids they
are very slight.   This is usually expressed by calling the
former "strong" acids and the latter "weak" acids.
In order to compare different acids in this respect it is,
of course, necessary to make use of some property which
can be quantitatively measured; in this way we can then
draw up a list of the relative strengths of acids.   Amongst
the numerous methods which have been employed the
following may be mentioned.

(1)   The two acids to be compared are allowed to
react with a base, all being added in *equivalent* quantities,
i.e. there is just base enough to neutralise either acid but
not enough to neutralise both.   Hence the two acids will
compete for the base and the one which takes most of it
is considered to be the stronger, or is said to have the
greater *avidity*.   [This experiment must, of course, be
performed in solution so that all the reacting substances
are kept in the system.   Formerly attempts were made to
compare the strengths of acids by distilling the salt of
one acid with the other acid;   this, of course, is not
legitimate since the more volatile acid is removed from
the sphere of action.   Thus, the fact that when a nitrate
is distilled with sulphuric acid, free nitric acid results,
is no proof that sulphuric acid is stronger than nitric.]
By this method it was shown that hydrochloric or nitric
acids are twice as "strong" as sulphuric.

(2)   Acids act as catalysts in many chemical changes
(such as in the inversion of cane sugar, the hydrolysis of
amides to acids and ammonia, the decomposition of
diazo-compounds, etc.) and their efficiency in this respect
varies very considerably with the nature of the acid.
If this efficiency is estimated by the rate at which the
changes proceed in presence of equivalent quantities of
various acids, it is found that the order of the efficiencies
is the same as the order obtained by the "division of
base" method mentioned above.

(3) The electric conductivities for equivalent quantities (i.e. equivalent conductivities, see Section 97) are found also to be approximately in the same order as the "strengths" measured by the foregoing methods.

[It was formerly supposed that the heats of neutralisation of acids, with a given base, gave an indication of the strengths of acids. This has been shown to be quite erroneous; thus hydrofluoric acid is one of the weakest acids when tested by the foregoing or other methods, yet its heat of neutralisation is greater than that of nitric, hydrochloric or sulphuric acids.]

It will be observed that all these methods merely give a relative "order of merit" to the acids. The results, moreover, depend to some extent on the dilution, so that in drawing up the list representing this order it is necessary to specify what particular dilution was employed. The whole conception of the "strengths" of acids and bases and the quantitative expression of their values can be placed on a much more satisfactory and intelligible footing by reference to the ionic dissociation hypothesis. In terms of this hypothesis, the "acidic" properties of acids are due to free hydrogen ions and the greater the concentration of these ions the stronger will be the acid. Therefore if we compare two monobasic acids at a given dilution and find that one is half ionised and the other is two-thirds ionised we say that the latter is the stronger. Since the degree of ionisation increases with dilution it is evident that, theoretically, all acids would be equally "strong" at infinite dilution, since they would then all be completely ionised.

Regarding the "strength" of an acid in this way, one may express the value quantitatively by the *dissociation constant* of the acid, $K = \dfrac{m^2}{(1 - m)\, V}$. Evidently this enables us to compare the strengths of acids even though the dilutions at which we make the experiments are different. The method is based however on the theory that the ionisation of the acid obeys the law of mass

action. This is quite true for weak acids but fails in case of strong acids. Consequently it is generally the custom to state the strengths of weak acids by means of their dissociation constants, whereas the "strengths" of the stronger acids are still often compared by the older methods, e.g. by their "avidities" for base.

It can be shown that the ratio of the avidities of two weak acids is practically the same as the ratio of the degrees of ionisation of the acids at the same dilution.

CHAPTER VIII

ELECTRO-CHEMISTRY (*continued*)

86. Galvanic cells. A galvanic cell may be regarded as a machine for converting chemical energy into electric energy. If plates of two different metals, say zinc and copper, are immersed in dilute sulphuric acid, each plate becomes charged with opposite kinds of electricity; the zinc becomes charged negatively and the copper positively. If now the two plates are connected by a metallic wire, the latter assumes peculiar properties; the temperature of the wire is raised, and a magnetic needle placed near the wire becomes deflected. Also, if two wires, connected with the two plates respectively, be dipped into a solution of potassium sulphate it will be found that the solution becomes alkaline round the wire connected with the zinc plate and acid round the other wire. These effects are explained by saying that an electric current is produced when the plates are connected by some conducting material; positive electricity flows from the copper to the zinc through the wire. In the solution in the cell changes are also taking place; zinc sulphate is formed and goes into solution and hydrogen appears on the copper. That is to say, the positive constituent of the sulphuric acid, hydrogen, travels towards the copper and the negative constituent (SO_4) towards the zinc; each of these constituents carries an electric charge, the hydrogen being positively charged and the SO_4 negatively charged. Positive electricity flows then in the solution from the zinc to the copper.

The *direction* of the current is taken as that in which positive electricity travels; of course, one may equally well say that a negative current passes in the opposite direction. Instead of zinc and copper in dilute sulphuric acid we can obtain electric currents by using various other pairs of metals and other liquids. Currents are also obtained, in a similar way, when plates of the same metal are immersed in solutions of the same substance (acid, salt or base) of *different concentrations*; or when one is immersed in a solution of an *oxidising agent* and the other in a solution of a *reducing agent*; or, again, when two plates of the same metal upon which different gases (e.g. hydrogen and chlorine or hydrogen and oxygen) are condensed are immersed in a solution of acid, salt or base. If two platinum plates are equally charged with hydrogen and immersed in dilute acid, no current is obtained on making connection; but if the plates are *unequally* charged, a current is produced. Another interesting case is that of a cell composed of two plates of the same metal in *different allotropic states* immersed in a liquid in which both forms are soluble, e.g. grey and white tin in a solution of $(NH_4)_2SnCl_6$. Here a current passes in the liquid from the less stable to the more stable form.

In a galvanic cell consisting of two metals such as zinc and copper or zinc and platinum, immersed in a dilute acid, there is a deposition of hydrogen on the plate which is not acted upon, i.e. on the plate which becomes positively charged. This reduces the electromotive force of the cell, hydrogen being nearer to zinc in the potential series (page 170). To prevent this "polarisation" of the plate, various devices are employed. A *Daniell's* cell consists of a zinc plate in dilute sulphuric acid and a copper plate in a strong solution of copper sulphate, the two being separated by a porous partition. Here, instead of hydrogen, copper is deposited on the copper plate.

In *Grove's* cell there is a platinum plate immersed in nitric acid and a zinc plate in sulphuric acid, the two being separated by a porous partition. No hydrogen is

here liberated at the platinum plate since it reduces the nitric acid to nitrous acid, etc.

In the *Leclanché cell* there is a zinc plate in a solution of ammonium chloride and a carbon rod round which is packed manganese dioxide; deposition of hydrogen on the carbon is thus prevented, the manganese dioxide becoming reduced to lower oxides. The *bichromate* cell has a zinc plate in dilute sulphuric acid and a carbon plate in a solution of chromic acid, or potassium bichromate and dilute sulphuric acid; instead of deposition of hydrogen on the carbon, the result is reduction of the chromic acid to chromium sulphate.

The *lead accumulator* consists of plates of lead immersed in dilute sulphuric acid and lead sulphate. This is charged by passing a current into it, when one of the lead plates becomes coated with lead peroxide and on the other reduced lead is deposited. When connection is now made between the plates, the reduced lead becomes dissolved as lead sulphate and the peroxide on the other plate is reduced to oxide, which then dissolves in the dilute sulphuric acid to sulphate. The changes may be represented as

$$2PbSO_4 + 2H_2O \rightleftharpoons Pb + PbO_2 + 2H_2SO_4.$$

[Galvanic cells are said to be *reversible* when the process which takes place in their working can be reversed when a current is passed through them in the opposite direction. The lead accumulator and Daniell's cell are reversible in this sense.]

The electric current obtained by means of any of these cells may be made to do work; by using a sufficient number of cells we could run a motor, or we could effect chemical decompositions, such as the breaking up of water into its elements. Or, we might cause the current to pass through a long thin wire and employ the heat evolved for the performance of work. The source of this electric energy is, mainly, the chemical reaction which takes place in the cell. [In the concentration cells

referred to, the source of energy is the *difference* in concentrations. That such a difference must represent a source of energy is evident when we remember that solutions of different concentrations have different vapour pressures and different osmotic pressures and that by means of these differences work can be obtained.]

87. *Relation between chemical energy and electric energy in a galvanic cell.* We can measure the change of total energy which occurs in a chemical reaction by causing the reaction to take place in a closed calorimeter and determining the heat evolved; call this H calories. Further, electric energy is measured by the product, electromotive force × quantity of electricity passing; the unit generally adopted is the volt-coulomb or *Joule*. The heat equivalent of one volt-coulomb is 0·2391 calories Therefore if E is the electromotive force and Q the quantity of electricity passing, the electric energy is EQ and the heat equivalent of this is $EQ \times 0\cdot2391$.

Now it was at one time supposed that the whole of the energy run down in the chemical change occurring in the cell appeared as electric energy; i.e. that

$$H = EQ \times 0\cdot2391. \quad \text{(This was called Thomson's rule.)}$$

In the Daniell's cell this is approximately true. Thus, the chemical change occurring when this cell is working may be represented simply as the replacement of copper by zinc, $CuSO_4 + Zn = ZnSO_4 + Cu$, and, from calorimetric determinations, it can be calculated that the heat change accompanying this reaction is + 50,130 calories. When this change is used to generate the electric current, for each gram atom of zinc dissolved, or of copper deposited, the quantity of electricity which passes is $2 \times 96,540$ coulombs (see Section 91). The electromotive force of a Daniell's cell is about 1·1 volt; the electric energy is therefore $1\cdot1 \times 193,080$ volt-coulombs, and the heat equivalent of this is $1\cdot1 \times 193,080 \times 0\cdot2391 =$ about 50,780, which agrees well with the calorimetric value.

But afterwards it was shown that the equivalence between chemical and electrical energy in the cell will only hold for particular cases. In other cells the electric energy may be either greater or less than the energy of the chemical change. It can be shown by thermodynamics that the electric energy is equivalent to the chemical energy only in cells whose electromotive force does not alter with temperature, as is the case with the Daniell's cell. If the electromotive force increases with rising temperature the electric energy is greater than the energy of the chemical reaction; in this case the cell cools in working, i.e. heat is *absorbed* from the surroundings. If the electromotive force diminishes with rising

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temperature, the energy of the chemical reaction is greater than the electric energy and heat is *evolved* in the cell.

88. *Electrolytic solution pressure.* The changes which take place in a galvanic cell with production of an electric current are very conveniently explained in terms of a theory, due to Nernst, which has briefly been referred to in Section 40. A substance in contact with a liquid is supposed to have, at a given temperature, a definite solution pressure in virtue of which it tends to go into solution, just as a liquid has, at a given temperature, a definite vapour pressure. In the case of a liquid, vaporisation continues until the pressure of the vapour in the space above is equal to the vapour pressure of the liquid and, if the vapour pressure in the space exceeds this, vapour will condense to liquid. Similarly, a solid substance placed in a liquid will go into solution until the osmotic pressure of the substance in solution is equal to the solution pressure; if the osmotic pressure exceeds this value, solid will be precipitated. In terms of the hypothesis of ionisation, we may extend this theory of solution pressure to metals and may suppose that in this case each metal has at a given temperature a definite *electrolytic solution pressure* in virtue of which it tends to throw itself into solution in the form of ions, and that this process will go on until the solution pressure is equal to the osmotic pressure of its ions in solution.

If, therefore, a plate of metal is placed in water, positively charged metallic ions will be thrown into the liquid; the latter will therefore become charged positively and the metal, which was previously neutral, will become negatively charged. But this negative charge on the plate will attract the positively charged ions in solution, this attraction opposing the solution tendency of the metal, so that the solution of the metal ceases as soon as these two forces balance one another. Since each ion is associated with an enormous electric charge, the entry of a very few ions into the solution will be sufficient to establish this state of equilibrium, and the quantity of

metal now present in solution is altogether too small to be detected by analytical means.

When a metal is placed in a solution of one of its salts it will behave similarly, provided that the osmotic pressure of the metallic ions already in solution is less than the solution pressure of the metal. If however the osmotic pressure of the ions already in solution exceeds the solution pressure of the metal, metallic ions will be deposited on the metal, thereby giving it a positive charge. There are therefore three possible cases, according as the osmotic pressure of the metallic ions is less than, greater than, or equal to, the solution pressure of the metal. In the last case nothing happens and the metal and solution remain uncharged.

Now the electrolytic solution pressures of the metals vary very considerably; those of magnesium, aluminium and zinc, for example, being great, whereas those of copper, gold and platinum are very small. A plate of zinc will become negatively charged when placed in even a very concentrated solution of zinc sulphate, the osmotic pressure of zinc ions being insufficient to overcome the solution pressure of the zinc; whereas a plate of copper immersed in a very dilute solution of copper sulphate becomes positively charged, since a very small osmotic pressure of copper ions is sufficient to overbalance the solution pressure of the metal.

In a Daniell's cell we have, as above stated, a plate of zinc in dilute sulphuric acid (or zinc sulphate), separated by a porous partition from a plate of copper in a solution of copper sulphate. The zinc ions go into solution, leaving the plate negatively charged, and copper ions are deposited on the copper plate, giving it a positive charge. But so long as the plates are disconnected nothing more happens, since the electrostatic attractions between the ions in solution and the charged plates, respectively, prevent further action. If now the two plates are connected by means of a wire, the positive charge of the copper plate neutralises the negative charge

of the zinc plate and, consequently, since the electrostatic attractions mentioned are thus removed, more zinc ions are enabled to go into solution and more copper ions are discharged on the copper plate. The result of this is that the two plates again become charged in the same manner as before and these charges are again neutralised through the wire, and so on. We have in this way a continuous flow of positive electricity from the copper to the zinc in the wire and from the zinc to the copper in the solution. In the wire the electricity is conveyed by the metal, whereas in the solution it is conveyed by the moving ions.

[Note that a current of positive electricity in one direction is equivalent to a current of negative electricity in the other direction; in a galvanic cell, a current may be produced just as well by removal of negative ions as by the production of positive ions. Thus we might construct a cell consisting of copper in copper sulphate solution and an inert plate (e.g. of platinum) in hydriodic acid. In the working of this cell, negatively charged iodine ions of the hydriodic acid would be discharged on the platinum plate, thereby giving it a negative charge, and becoming neutral iodine. A positive current here enters the liquid due to the removal of negative ions, whereas in the Daniell's cell the positive current entering at the zinc plate was due to the production of positive ions.]

In a *concentration cell* we may have two plates of the same metal immersed in two solutions of the same electrolyte having different concentrations, the two solutions being connected, e.g. by a conducting liquid. Here the solution pressure of the metal is the same in both and in each the solution pressure is opposed by the osmotic pressure of the ions of the metal in solution. But since the solutions have unequal concentration, it is evident that the solution pressure of the metal is more opposed in one solution than it is in the other. Hence the electromotive force will be different in the two and if the plates are connected by a wire, metallic ions will

dissolve off the plate in the weaker solution and will be deposited on the plate in the stronger solution. A positive current thus passes in the *solution* from the weaker to the stronger and in the *wire* from the stronger to the weaker. The result is that the weaker solution becomes stronger and the stronger solution weaker; when the strengths of the two solutions become equal the current ceases.

In an *oxidation and reduction cell* we have two plates of the same metal, one immersed in a solution of an oxidising agent and the other in a solution of a reducing agent, the two solutions being connected, for example, by a solution of some inert electrolyte. When the two plates are connected by a wire, a positive current flows from the oxidising agent to the reducing agent in the *wire* and from the reducing agent to the oxidising agent in the *solution*. Suppose, for example, that we have two platinum plates, one of which is immersed in a solution of ferric chloride and the other in a solution of stannous chloride, the two solutions being connected by means of a solution of common salt. On connecting the plates by a metallic wire, the stannous salt will become stannic and the ferric salt will become ferrous. The chemical change usually written

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

may be regarded simply as

$$2\overset{...}{Fe} + \overset{..}{Sn} = 2\overset{..}{Fe} + \overset{....}{Sn},$$
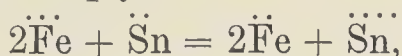
i.e. as a transference of two positive charges from two atoms of trivalent iron to one atom of bivalent tin, and this transference here takes place *through the metallic wire*.

89. *Electrode potentials.* The electromotive force of a galvanic cell, as directly measured, is the difference of potential between the two wires connecting the plates. In the whole arrangement there are four surfaces of contact each of which gives rise to an electromotive force, namely (*a*) the contact between the two metals, (*b*) that between the two solutions, and (*c*) that between

each electrode and its solution. The first two may, in most cases, be neglected as they are insignificantly small in comparison with (c).

The difference of potential between a metal electrode and the solution in contact with it is called the *electrode potential* of the metal; it is measured by the work done in carrying unit quantity of electricity between the electrode and solution. In terms of the theory above indicated, the electrode potential is a measure of the work done in the formation or discharge of an ion. Evidently at an electrode which is producing ions, the difference of potential will be greater as the concentration of the ions already in solution is *smaller*; whereas at an electrode upon which ions are being discharged, the difference of potential will be greater as the ionic concentration in solution is *greater*. Thus, in a Daniell's cell the zinc will have a greater tendency to go into solution as zinc ions the weaker the solution of zinc sulphate in which it is immersed; whereas the tendency of copper ions to be discharged on the copper plate will be greater as the solution of copper sulphate is stronger.

In order therefore to compare the electrode potentials of various metals in contact with their solutions, we must decide upon some standard concentration of the solutions. For this purpose it is customary to employ normal solutions of the salts, i.e. those containing one gram equivalent of the metal per litre. [The nature of the acidic radicle is in most cases immaterial, i.e. the electrode potential is practically the same whether we use sulphate, nitrate, chloride, etc.; exceptions may however occur, e.g. when cyanides are employed.]

89 a. In terms of the theory of electrolytic solution pressure, the electrode potential will depend on the difference between the electrolytic solution pressure (P_1) of the metal and the osmotic pressure (P_2) of its ions in solution. The exact relation can be calculated if the electrode is a *reversible* one, i.e. if the process taking place in its action can be reversed by passing a current in the opposite direction.

From the fact that the gaseous laws are applicable to solutions, we can calculate the maximum work obtainable when one mol of metal of solution pressure P_1 dissolves in a solution to the osmotic pressure P_2; we may regard it as the same as if the metallic ions expanded from P_1 to P_2. This work is the same as it would be for a gas, namely $RT \log_e \dfrac{P_1}{P_2}$ (see Section 12). In a galvanic cell this amount of work can be obtained entirely in the form of electric energy. If now one molecule of the metal produces one ion which is n valent, the quantity of electricity passing from electrode to solution will be $n \times 96{,}540$. The electric energy is the quantity of electricity multiplied by the difference of potential (E) and hence, since the osmotic work is equal to the electric work,

$$E \times 96{,}540 \times n = RT \log_e \frac{P_1}{P_2}.$$

Adjusting units and using ordinary logarithms, the value of E in volts, at 18°, becomes

$$E = \frac{\cdot 0577}{n} \log \frac{P_1}{P_2},$$

a formula which is of much service in electro-chemical calculations.

The electromotive force of a galvanic cell will be the sum of, or the difference between, the two electrode potentials, according as they act in the same or in opposite directions. If we wish to determine the *single* electrode potential of a metal it is, of course, necessary to have some *standard* electrode of *known* electromotive force for comparison. We can then construct a galvanic cell in which one electrode is the known standard and the other is the metal to be determined, each being in a normal solution of its salt. This standard electrode is generally called a "normal" electrode. A convenient one which is easily reproduced is the calomel electrode; it consists of a vessel containing mercury covered with a layer of calomel and filled with a normal solution of potassium chloride. The difference of potential between the mercury and solution in this electrode has been estimated as 0·56 volt at 18°. If we accept this value, we can at once determine the absolute single potentials of other metals and also their solution pressures. Unfortunately, however,

there is some uncertainty with regard to the exact value, which has been determined by indirect methods. [One such method depends on the fact that the surface tension of mercury in contact with an electrolyte changes when the difference of potential between the mercury and solution changes.]

Consequently, it is generally the custom to adopt an arbitrary standard for comparison, since, after all, it is mainly the relative values of the electrode potentials which are of importance. The arbitrary standard usually employed is the *hydrogen electrode*, which, for this purpose, is assumed to have zero potential. It consists of a plate of platinised platinum saturated with hydrogen at 760 mm. and partly immersed in a normal solution of sulphuric acid.

The following are the electrode potentials of some of the metals; the numbers represent the electromotive force in volts when the metals are in normal solutions of their salts:

$$\text{Mg} + 1 \cdot 48; \text{ Al} + 1 \cdot 27; \text{ Zn} + 0 \cdot 77; \text{ Cd} + 0 \cdot 42; \text{ Fe} + 0 \cdot 33;$$
$$\text{Pb} + 0 \cdot 15; \text{ H} \pm 0; \text{ Cu} - 0 \cdot 329; \text{ Ag} - 0 \cdot 77.$$

A galvanic cell made up of any two of these metals in normal solutions of their salts will have an electromotive force equal to the algebraic difference between the electrode potentials. Thus for the combination, zinc in zinc sulphate, copper in copper sulphate, we shall have an electromotive force of $0 \cdot 77 - (- 0 \cdot 329) = 1 \cdot 099$ volts. For iron, lead, it will be $0 \cdot 33 - 0 \cdot 15$ volt, and so on. That is to say, we reverse the minus sign and add the numbers if the electromotive force is in the same direction at both electrodes; whereas if it is in opposite directions we subtract one value from the other.

This series of electrode potentials corresponds in a general way with that which the older chemists called the *electrochemical series*; this was a list of the elements arranged in the order in which one element usually displaced another from its compounds. This list was

necessarily only approximate and qualitative in nature, whereas the series of electrode potentials expresses the same idea in a precise and quantitative way. Evidently a metal with a higher positive electrode potential will displace one having a lower value from its salts, provided, of course, the experiment is made in solutions of the same ionic concentration. A metal whose electrode potential is positive should therefore replace hydrogen from acids, whilst one with a negative value should be precipitated from its salts by hydrogen.

The old terms "noble metal" and "base metal" are still much in use; they refer in a loose and general way to the ease with which the metal is reduced or oxidised. The above potential series evidently expresses this meaning in a more definite way, the higher the positive potential the "baser" the metal and the greater the negative value of the potential the more "noble" is the metal.

90. Electrolysis. Substances which are capable of conducting the electric current are divided into two classes. The *first class* includes the metals and certain forms of carbon, selenium, etc. In these the electricity is conveyed without any visible transportation of matter and the material of the conductor suffers no permanent change. Its physical properties are, it is true, altered during the time in which the electricity is passing, since its temperature rises and it has the property of affecting a magnet; but as soon as the current ceases the material regains its former properties.

Conductors of the *second class* are always compound substances and, in them, the current is conveyed by the constituent parts, definite chemical changes occurring. They are, in nearly all cases, either acids, salts or bases. In order that they may convey the current they must be either *dissolved* in a suitable solvent or must be in the *fused* state*. The most suitable solvents for this purpose

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* There are exceptions to this, since certain solids (e.g. heated metallic oxides) which can convey the current appear to undergo

are those having a high dielectric constant, such as water; liquid ammonia, liquid sulphur dioxide and liquid hydrocyanic acid all serve in this way as solvents although not nearly so well as water; whereas liquid hydrogen sulphide, benzene, toluene, etc. do not serve at all. A solution of potassium chloride in water is a remarkably good conductor, whereas the same salt dissolved in liquid hydrogen sulphide does not conduct at all.

Conductors of the second class are called *electrolytes* and the conduction of the electric current by them, with the resulting chemical changes, is called *electrolysis*. In order to bring about electrolysis in a solution of an electrolyte the most usual way is to dip into the solution two metal plates, or wires, which are connected, respectively, with the plates in a galvanic cell, or series of cells. These two plates, or terminals of the wires, which dip into the solution are called *electrodes*; the one which is connected with the positively charged plate of the galvanic cell is called the *anode*, and the one connected with the negatively charged plate is called the *cathode* (or kathode).

As soon as the electrodes are dipped into the solution, the current passes through the solution from the anode to the cathode, being conveyed by the electrically charged constituent parts of the electrolyte. These electrically charged constituent parts are called *ions*; the one which is negatively charged, and which moves towards the anode, is called the *anion*, and the one positively charged, which moves towards the cathode, is called the *cation* (or kation).

In such an arrangement we have the galvanic cell in which the electric energy is generated, and the electrolytic cell in which the chemical decompositions are effected. Each consists of two plates in a solution of an electrolyte and in each anions move in one direction and cations in the other direction. There is, in fact, no essential difference between them as regards construction

decomposition in the process; also, gases can convey the current and the process appears to be analogous in some respects to the conduction in liquids ("ionisation" of gases, see Section 100).

and by altering the conditions they may be interchanged. Thus, for example, a lead accumulator is an electrolytic cell when it is being charged and a galvanic cell when it is discharging. For this reason it is now the custom to call each of the plates an *electrode* whether it is in the galvanic cell or in the electrolytic cell. That electrode towards which the positively charged ions travel is always the cathode and the one towards which
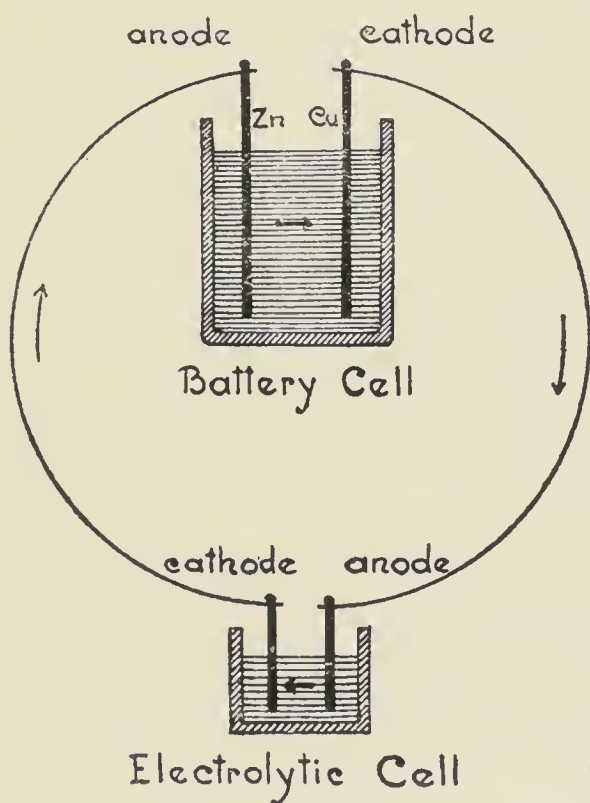
the negatively charged ions travel is always the anode, whether these electrodes are in the galvanic cell or in the electrolytic cell. Thus in a Daniell's cell, when used to generate a current, the zinc plate is called the anode and the copper plate the cathode.

This method of naming the plates in a galvanic cell is far better than the older one, since the latter often led to confusion. Formerly, the zinc was called the positive plate and the copper the negative plate, and the terminals

of the wires connected with these plates were called the
negative electrode and positive electrode, respectively.

At the places where the current enters or leaves a
solution of an electrolyte, definite chemical changes
occur. The ions which travel towards the electrode may
be discharged there, appearing as the neutral (uncharged)
form of the substance. Such products are spoken of as
primary products of electrolysis. Or, the primary products
may immediately undergo chemical changes either of
themselves or by reaction with the solvent; the substances
actually obtained in this way are called *secondary products*.

91. *Faraday's law.* Faraday established the following
two important laws, the second of which is usually spoken
of as "Faraday's law."

(1) The amount of decomposition effected in an
electrolytic cell is directly proportional to the quantity
of electricity which passes.

(2) The quantities of different substances which are
liberated or deposited during electrolysis by the same
quantity of electricity are proportional to their *equivalent*
weights.

These laws are universally true and are independent
of concentration of the solution, temperature, size of
electrodes, etc. [Note that these laws say nothing about
the quantity of electric *energy* required to bring about
the decompositions; many mistakes were formerly made
by confusing the two things.]

It is evident from the first law that we may employ
electrolysis for the measurement of the quantity of
electricity which passes through a circuit; the electro-
lytic cell when so employed is called a *voltameter*.

In order to illustrate the second law, imagine that
the same current is passed for the same time successively
through solutions of (*a*) dilute sulphuric acid, (*b*) silver
nitrate, (*c*) a cupric salt, (*d*) a cuprous salt, in separate
cells. Suppose that one gram of hydrogen is obtained at
the cathode in the first cell (*a*); then at the cathodes in

the other cells we should obtain (in round numbers) 108 grams of silver in (b), 31·75 grams of copper in (c) and 63·5 grams of copper in (d). The same quantity of electricity therefore accompanies the liberation of twice as much copper from the cuprous salt as it does from the cupric salt.

Careful experiments have shown that the quantity of electricity which accompanies the liberation of one gram equivalent of any element, or radicle, is 96,540 coulombs. [The coulomb is the practical unit of electric *quantity*; it is the quantity of electricity which accompanies the liberation of 0·001118 grams of silver from silver nitrate.] This quantity of electricity—96,540 coulombs—is called a *faraday* and is usually denoted by the letter F.

92. *Polarisation.* If a dilute solution of sulphuric acid is electrolysed, using platinum electrodes, we obtain hydrogen at the cathode and oxygen at the anode. These products are principally evolved as gases, but a small part of each is adsorbed on the electrodes as a condensed layer on the surface. If the cell be disconnected from the battery and the two plates are connected with a galvanometer, it will be found that a current passes through the galvanometer from the plate on which oxygen is deposited to the plate on which hydrogen is deposited, i.e. in the opposite direction to the original current which produced the electrolysis. The original electrolytic cell has now become a galvanic cell in which the electrodes are oxygen and hydrogen. If, in the electrolysis of the dilute acid, we begin with a very small electromotive force we find that although at first a current passes, it almost immediately drops to nothing (or nearly so), the back electromotive force of the oxygen-hydrogen cell opposing the original current. On increasing the electromotive force more current passes for the moment, but again nearly stops. This continues until the applied electromotive force reaches about 1·11 volts; beyond this the electrolysis proceeds normally, i.e. the applied

electromotive force is able to overcome the electromotive force of the oxygen-hydrogen cell. [The reason why the current does not entirely stop when the smaller electromotive force is applied, is that the oxygen and hydrogen layers gradually dissolve off the electrodes, i.e. the polarisation of the electrodes slowly disappears spontaneously; the small current which is able to persist in this way is spoken of as the *residual current*.]

With other electrolytes similar polarisation effects occur. In a reversible cell, such as the Daniell, if we apply to it an electromotive force which just balances its own, in the opposite direction, no current will pass; but if this applied electromotive force is ever so slightly increased copper will begin to dissolve off the copper electrode and zinc will be deposited on the zinc electrode, the current now passing in the liquid from copper to zinc. If, on the other hand, the applied electromotive force is less than that of the Daniell's cell, copper deposits on the copper electrode and zinc dissolves off the zinc electrode, the current passing in the liquid from zinc to copper.

The lead accumulator is another example. Cells in which the products of electrolysis accumulate on the electrodes and are then used to generate a current in the opposite direction are called *secondary cells* and a battery of them is called a secondary battery.

93. *Decomposition voltage.* For each electrolyte, of a given concentration, there is a definite electromotive force required in order to produce continued electrolysis, when indifferent electrodes are employed. This electromotive force is called the decomposition potential or *decomposition voltage* of the electrolyte. It evidently consists of two parts, one depending on the work done at the cathode and the other on that done at the anode. In the Daniell's cell in action, work is done at the anode by metallic zinc going into solution as ions, and at the cathode by copper ions being discharged as neutral metal; conversely, if we pass a sufficient current in the

opposite direction an equal amount of work is needed to reverse these changes. Now the electromotive force of the cell can be calculated as the algebraic difference between the electrode potentials. Consequently, the electromotive force required to reverse the process can be calculated in a similar way. If, for example, we electrolyse a solution of zinc sulphate, using some indifferent metal (e.g. platinum) as cathode, some metallic zinc will begin to deposit on the cathode, and as soon as this happens we have, practically, a zinc electrode in a solution of zinc sulphate. This will, of course, yield an electromotive force in the opposite direction to that used in electrolysing the solution. If the solution is of normal strength, this opposing electromotive force will be 0·77 volt, and if we wish to continue the electrolytic deposition of the zinc solution, we shall have to apply an electromotive force at least equal to this. This minimum electromotive force required to continuously discharge the metallic ions is called the *discharge potential* of the metal. It is evidently equal to the electrode potential as above defined and it will, of course, depend on the strength of the solution employed. The discharge potentials of *anions* can also be calculated. For normal solutions, the following values have been obtained:

$$I - 0{\cdot}52; \quad Br - 0{\cdot}99; \quad Cl - 1{\cdot}35; \quad SO_4 - 1{\cdot}9.$$

Knowing the discharge potentials of anion and cation we can at once calculate the minimum electromotive force which will be required to produce continued electrolysis; this minimum electromotive force is called the *decomposition potential* or *decomposition voltage*.

Thus for zinc bromide, in normal solution, we shall require an electromotive force of 0·77 + 0·99 volts. We here add the two numbers given in the list, reversing the negative sign of the anion, since the electromotive force required is in opposite directions at the two electrodes. Similarly, for normal hydrochloric acid we shall require 0 + 1·35 volts. For cupric chloride the value will be

$- 0.329 + 1.35 = 1.02$ volts. [We do not reverse the negative sign for copper, since the required electromotive force is in the same direction at both electrodes, i.e. the discharge of copper ions from its normal solution *yields* an electromotive force instead of requiring one.]

These discharge potentials are sometimes spoken of as *electro-affinities* since they may be regarded as a measure of the work necessary to separate the atom from its electric charge.

94. These principles are practically applied in *electrolytic separation*. If a mixture of different salts is electrolysed, using a gradually increasing electromotive force, it is often possible to effect a separation of the metals if their discharge potentials are sufficiently different. Thus, in solutions of normal strength, the metals would be precipitated in the inverse order of the list given on page 170; silver before copper, copper before cadmium, and so on. But the electromotive force required to discharge a metal depends, as above stated, on the concentration of its ions in solution and, as the metal is deposited, its ionic concentration becomes reduced. Hence if we electrolyse solutions of two metals whose discharge potentials are very close together, it may happen that when a certain quantity of the first metal has been deposited, the electromotive force necessary to deposit the remainder may reach the discharge potential of the second metal and the two metals will then be deposited together.

In the purification of copper, the impure metal is made the anode in the electrolysis of copper sulphate solution, the cathode being made of the pure metal. Using a small electromotive force, pure copper is deposited at the cathode and the crude metal dissolves at the anode. Iron, zinc, etc. remain dissolved whilst gold, silver, bismuth or lead are deposited as " anode mud."

From what has been said above it will be evident that the actual products obtained at the electrodes

during electrolysis of mixed electrolytes need not necessarily be the substances by whose ions the current was principally conveyed through the liquid. There will be various ions round the electrodes and that ion will be first discharged whose discharge potential, at the given concentration, is least.

95.   Examples and applications of electrolysis. A few examples will be given here which illustrate the principal results obtained when some of the commoner substances are electrolysed, reference being made also to some of the practical applications of electrolysis.

Hydrochloric acid.   At the cathode hydrogen is evolved and at the anode both chlorine and hydroxyl ions may be discharged. The stronger the acid used the greater will be the proportion of chlorine and, with very strong solutions, the chlorine liberated at the anode is approximately equivalent to the hydrogen at the cathode. [This is a familiar lecture experiment, the gases being collected in measuring tubes. A carbon anode is employed and the solution is previously saturated with chlorine, so that the chlorine evolved on electrolysis does not dissolve.] With weaker acid the Cl and (OH) ions may react giving rise to oxygen, hypochlorous acid, chloric acid, etc. If the anode is of platinum it may be, to some extent, attacked by the chlorine.

Copper sulphate solution electrolysed with platinum electrodes gives metallic copper at the cathode. At the anode the SO_4 ions are primarily discharged, but being incapable of existence in the uncharged state, they at once break up into sulphur trioxide, which dissolves as sulphuric acid, and oxygen which is evolved as gas. If however a copper anode is used in place of platinum, the SO_4 attacks the copper again forming copper sulphate, so that the total amount of copper in solution remains unchanged.

Sulphuric acid.   The products actually obtained when *dilute* sulphuric acid is electrolysed, with platinum

electrodes, are hydrogen at the cathode and an equivalent quantity of oxygen at the anode. [Under certain conditions the oxygen is partly ozonised.] Here the SO_4 primarily liberated at the anode breaks up as in the previous example, giving sulphuric acid and oxygen.

If the acid is more concentrated, the volume of oxygen liberated is diminished and, in the liquid, persulphuric acid, $H_2S_2O_8$, is formed. Its formation might be explained either by supposing that two bivalent SO_4 ions each lose one of their charges, becoming the bivalent ion $(S_2O_8)''$ of persulphuric acid; or, that the sulphuric acid ionises first as $2\overset{\cdot}{H} + (HSO_4)'$ and that the latter ions condense to $H_2S_2O_8$ with loss of their electric charges. If a potassium salt is present potassium persulphate, being sparingly soluble, may separate round the anode.

Sodium sulphate. In dilute solution, using platinum electrodes, the actual products obtained are hydrogen at the cathode and an equivalent amount of oxygen at the anode, whilst the liquid round the cathode becomes alkaline and that round the anode becomes acid.

The old view was that the salt is broken up by the electric current into acid and base, while, at the same time, water is broken up into oxygen and hydrogen. This explanation would involve a contradiction to Faraday's law (see below), and the more modern theory is that the primary products are $2\overset{\cdot}{N}a$ at the cathode and $(SO_4)''$ at the anode. The Na ions are discharged, giving metallic sodium which immediately reacts with the water yielding caustic soda and hydrogen, whilst the $(SO_4)'$ ion on discharging breaks up into sulphur trioxide and oxygen.

In view of more recent work, however, even this explanation has been modified. It is probable that in this, and in many other cases when salts are electrolysed in aqueous solution, the *water* is primarily electrolysed. Although the current is mainly conducted through the liquid by the Na and SO_4 ions, it does not follow that these are the primary products discharged at the electrodes.

More probably, in the present case, hydrogen from the water is discharged at the cathode, leaving an excess of (OH) ions in solution, which accounts for the alkalinity round the cathode. At the anode (OH)′ ions are discharged but break up into water and oxygen, and excess of hydrogen ions in the solution accounts for the acidity.

Sodium chloride. As in the last example we obtain caustic soda and free hydrogen at the cathode. At the anode chlorine is liberated and dissolves in the water, or partly reacts with the water as above indicated. If these principal products—caustic soda and chlorine—obtained in solution at the electrodes are allowed to mix together we obtain sodium chloride and hypochlorite, or sodium chloride and chlorate, according to conditions of concentration and temperature. This method is largely employed for the preparation of hypochlorites and chlorates.

If in the electrolysis of solutions of sodium or potassium salts we employ a mercury cathode, the alkali metal itself is obtained in form of an amalgam with mercury. This may then be decomposed by water, giving a solution of caustic alkali. In the Castner-Kellner process, chlorine and caustic soda are prepared from common salt by this method.

The electrolysis of *fused* metallic chlorides, hydroxides, etc. is employed in the preparation of various metals: e.g. calcium, lithium, and magnesium from the chlorides, potassium and sodium from the hydroxides, aluminium from the oxide dissolved in fused cryolite, etc.

Silver salts. Silver nitrate, in dilute solution, electrolysed with platinum electrodes yields metallic silver at the cathode and the radicle NO_3 at the anode. The NO_3 then reacts with water giving nitric acid and oxygen $[2NO_3 + H_2O = 2HNO_3 + O]$. If the anode is made of metallic silver, the NO_3 attacks the metal re-forming silver nitrate so that the strength of the solution remains unchanged. [On electrolysis of strong solutions of silver nitrate under suitable conditions, black shining crystals are obtained at the anode; these were formerly supposed

to be peroxide of silver, but they appear to have the empirical composition Ag_7NO_{11}.]

The silver deposited at the cathode is usually crystalline and incoherent and is therefore unsuitable for electroplating. For the latter purpose a solution of silver cyanide in excess of potassium cyanide is employed, which gives a white coherent deposit. This solution must be regarded as containing the complex ions $[Ag(CN)_2]'$, for reason given in Section 81. But some silver cations are also present, since the formation of the complex salt is formed by the reversible reaction

$$KCN + AgCN \rightleftarrows K[Ag(CN)_2].$$

On electrolysis, the current is conveyed in the solution, mainly by the K and $[Ag(CN)_2]$ ions. At the cathode however Ag ions which are in the liquid are discharged in preference to K ions, in spite of their small concentration, owing to the great difference in the discharge potentials. At the anode the $Ag(CN)_2$ ions are discharged and, acting on the silver electrode, yield AgCN, which then dissolves in the excess of potassium cyanide as $K[Ag(CN)_2]$.

Electro-gilding may be similarly explained, the cyanide solution containing the complex salt $K[Au(CN)_4]$.

Lead salts, on electrolysis, yield, under suitable conditions, metallic lead at the cathode and lead peroxide at the anode. If nitric acid is previously added to the solution, the deposition of the metal at the cathode is prevented and the whole of the lead may be obtained at the anode in the form of peroxide.

If a solution of caustic soda is electrolysed using a *tin* anode the metal dissolves as stannate and from this solution metallic tin may be separated electrolytically at the cathode when the concentration is sufficient. In this way tin is recovered from tin plate (iron coated with tin).

Organic acids. These, as a rule being weak acids, are slightly ionised at moderate dilution; hence the sodium salt is usually employed for electrolysis. The most

typical change under favourable conditions may be represented in the case of a monobasic acid as

$$2R . COOH \longrightarrow R_2 + 2CO_2 + H_2.$$

Hydrogen is evolved at the cathode and the negative ion $R . COO$, which goes to the anode, splits up into carbon dioxide and the univalent radicle R; the latter however, being incapable of existence as such, appears as the molecule R_2. Sodium acetate, for example, yields at the anode a mixture of carbon dioxide and ethane C_2H_6. Similarly, cyanacetic acid, $CH_2(CN) . COOH$, yields at the anode carbon dioxide and $.CH_2CN$, the latter then appearing as succinonitrile, $CH_2CN . CH_2CN$.

Dibasic acids behave likewise, but the radicle being capable of separate existence appears as such; thus, succinic acid, $C_2H_4(COOH)_2$, yields ethylene and fumaric acid, $C_2H_2(COOH)_2$, yields acetylene.

The results obtained on electrolysis of organic acids depend considerably upon the conditions and changes other than the typical ones mentioned may occur. Propionic acid, $C_2H_5 . COOH$, for example, yields not only butane, C_2H_{10}, but a large proportion of ethylene and some ethyl propionate.

96. *Electrolytic oxidation and reduction.* It is evident that the products of electrolysis at the anode and cathode may act as oxidising agents and reducing agents respectively, and electrolytic methods are now largely employed for oxidations and reductions in technical processes. As regards electrolytes, oxidation processes may be regarded as either those consisting in the increase in the number of positive charges, or the decrease of negative charges, on an ion; reduction processes being the converse. In the case of non-electrolytes, such as most organic compounds, it is best to regard the process of oxidation as consisting in the relative increase of oxygen or other negative element, and reduction as the relative increase of hydrogen or other positive element.

The substance to be oxidised or reduced is usually

confined in a porous vessel in order to prevent diffusion, and in it is placed the anode or cathode respectively of an electrolytic cell in which some acid, salt or base is being electrolysed.

In bringing about electrolytic reductions or oxidations, the nature of the electrode is of much importance; much better reduction results are usually obtained, for example, with a lead cathode than with a platinum cathode. This may be explained by the fact that the surface of the electrode becomes supersaturated with hydrogen and the reduction is then much more effective. It has already been indicated, in Section 89, that the electromotive force or "discharge potential," necessary to discharge hydrogen from a solution containing a given concentration of hydrogen ions, has a definite value at a given temperature, under normal conditions. But it often happens that a much greater electromotive force than this is required, owing to the fact that the electrode becomes supersaturated.

The additional electromotive force required in this case is spoken of as a *supertension* or over-voltage. Evidently more energy is associated with its discharge than when the electrode is charged only to its normal potential and the greater reducing efficiency is attributed to this. Platinised platinum plates show this phenomenon very slightly, polished platinum more, and with tin, lead and mercury it is considerable. Similar phenomena are observed at the anode; oxygen over-voltage is greater for smooth platinum than for platinised platinum and the latter is greater than for iron or nickel.

Amongst electrolytic oxidation processes employed technically may be mentioned (a) the liberation of halogens. For example, bromine is separated from a mixture of chloride and bromide by suitably adjusting the electromotive force, bromine ions being more easily discharged than chlorine ions. (b) The oxidation of anthracene to anthraquinone; the process works more rapidly in presence of a catalyst such as chromic acid or cerium sulphate. (c) The preparation of iodoform. Here, instead

of free iodine, as in the ordinary mode of preparation, one can use an iodide; a mixture of alcohol (or acetone) with potassium iodide and alkali is electrolysed and the iodine liberated at the anode then acts in the usual way. In the ordinary mode of preparation a large proportion of the iodine is wasted, being converted into iodide, but in the electrolytic process it is liberated as required. (d) The conversion of manganates to permanganates. The change which occurs may be represented as

$$2K_2MnO_4 + 2H_2O = 2KMnO_4 + 2KOH + H_2,$$

(e) the conversion of sulphates to persulphates, (f) carbonates to percarbonates.

Examples of electrolytic reduction processes are (a) the reduction of nitrobenzene to aniline, (b) quinone to hydroquinone, (c) nitrates to ammonia, or to nitrites, (d) the reduction of uric acid, xanthine, etc., (e) camphor to borneol, and (f) pyridine to piperidine.

97. Electrolytic conduction. When an electric current passes through a conductor, the strength of the current depends directly on the difference of potential between the ends and inversely on the *resistance* of the conductor, or $C = \dfrac{E}{R}$ (Ohm's law). The *specific resistance* (R) of a conductor is the resistance (in ohms) of one centimetre cube of it when the resistance is taken between opposite faces; the reciprocal of this $\left(\dfrac{1}{R}\right)$ is called the specific conductivity (K). This number divided by the equivalent concentration is called the *equivalent conductivity*. Thus, if c is the equivalent concentration (i.e. the number of gram equivalent weights per c.c.) the equivalent conductivity is $\dfrac{K}{c}$. In order to determine the equivalent conductivity, the solution is placed in a cell in which are two platinised platinum electrodes and which is kept at a constant temperature; the resistance is then determined

by the usual Wheatstone's bridge arrangement, using an alternating current in order to eliminate the effects of polarisation. To obtain the specific resistance, the resistance obtained is multiplied by a factor called the "cell constant," which has been previously determined. The reciprocal of the specific resistance is then divided by the equivalent concentration of the solution or, what is the same thing, the specific conductivity is multiplied by the volume of the solution (in c.c.s) which contains one equivalent weight of the electrolyte.

In the case of strong monobasic acids, monacid bases and binary salts, such as potassium chloride, it is found that the equivalent conductivity increases as the dilution increases, at first rapidly and afterwards more slowly, up to a certain limit beyond which it becomes practically constant. Beyond this limit the *equivalent* conductivity is independent of the concentration, the *specific* conductivity being proportional to the concentration. If we compare the values of the equivalent conductivities of various binary electrolytes at this dilution, where the values become constant, it will be found that each can be represented as the sum of two quantities, one depending on the cation and the other on the anion (Kohlrausch's law). These quantities may be called the *ionic conductivities* since, according to theory, the current is conveyed only by the ions. The cations convey positive electricity in one direction and the anions convey negative electricity in the opposite direction. The whole current is therefore conveyed by both ions independently, positive electricity flowing in one direction being equivalent to negative electricity flowing in the opposite direction. The conductivity of an electrolyte will evidently depend on the *number* of ions, the *charge* they carry and the *speed* with which they move. If for the sake of simplicity we consider only binary electrolytes, composed of two univalent ions, at such a dilution that they are completely ionised, it is evident that, since the charge on each ion is equal, we may express the equivalent conductivity as

$U + V$, where U and V are numbers proportional to the speed of the cation and anion respectively. In other words, we may, by using appropriate units, express the equivalent conductivity of a completely ionised binary electrolyte as the sum of the speeds of its ions.

If however the electrolyte is not completely ionised, the equivalent conductivity will be less than $U + V$. Suppose m is the degree of ionisation (see Section 76), the equivalent conductivity will be $m\,(U + V)$, since only the ionised part conveys the current. Evidently then we may determine the degree of ionisation at a particular dilution (v) by measuring the equivalent conductivity at this dilution and again at infinite dilution (i.e. at a dilution at which it is completely ionised). Let C_v be the equivalent conductivity at a dilution v and C_∞ that at infinite dilution; we have then $C_v = m\,(U + V)$ and $C_\infty = U + V$. Hence $m = \dfrac{C_v}{C_\infty}$.

In case of weak electrolytes, C_∞ is determined indirectly (see below).

98. *Migration of ions.* If both ions move at the same rate, the conveyance of the current in solution will be shared equally between the two ions, since the charges they carry are equal; of the total quantity of electricity transported one-half will be conveyed by the cation and one-half by the anion. This is nearly the case with potassium chloride, the $\overset{.}{\mathrm{K}}$ and Cl' ions moving with almost the same speed. But in most electrolytes the speeds differ considerably and in consequence of this it is found that, after electrolysis has proceeded for a certain time, the concentrations of the solution round the cathode and anode have become unequal.

Suppose, for example, that the cation moves faster than the anion, it is evident that in a region round the cathode more cations will enter the region and fewer anions will leave the region, in a given time. Whereas in a region round the anode fewer anions will enter the region

and more cations will leave it. Hence the solution round the cathode will become stronger than that round the anode.

There is no contradiction to Faraday's law in this; for each cation liberated at the cathode there will always be an equivalent quantity of anion liberated at the anode. Suppose, in the case of a binary electrolyte consisting of two univalent ions, the cation moves three times as fast as the anion and suppose that, in a certain interval of time, three cations move away from the anode; three anions will be left without partners and will be discharged at the anode. At the same time three cations will enter the region round the cathode and three cations will be discharged at the cathode. But simultaneously one anion will move away from the cathode, leaving one cation without a partner which will be discharged at the cathode; one anion will enter the anode region and one anion will be discharged at the anode. On the whole then, four ions will have been discharged at each electrode while the solution round the anode has lost three anions, and three cations while that round the cathode has lost one cation and one anion. It is easy to see that the loss of concentration in the region round each electrode is proportional to the speed of the ion which moves *away from* that region; i.e. the loss at the cathode region is to that at the anode region as the speed of the *anion* is to the speed of the *cation*.

Thus by determining the loss of concentration round the cathode and anode we can find the ratio between the speeds of anion and cation. Calling the speed of the cation U and that of the anion V, the fraction of the total current carried by the cation will be $\dfrac{U}{U+V}$ and the fraction carried by the anion will be $\dfrac{V}{U+V}$. These fractions (first determined by Hittorf) are called *transport numbers* or *migration ratios*.

Measurement of the equivalent conductivity at "infinite dilution" gives us the sum of the ionic conductivities

and by determination of the transport numbers we find the ratio of these conductivities; hence we can calculate the conductivity due to each ion. The number obtained for each ion depends on the temperature, but is independent of the nature of the other ion. The following are some of the values at 18°:

Na 43·6; K 64·7; Ag 54; NH_4 64; H 318; OH 174; Cl 65·4; Br 67·6; I 66·4; NO_3 61·8.

Knowing these numbers, we can calculate the equivalent conductivities of various binary electrolytes, at infinite dilution, by simply adding the values together. Thus, the equivalent conductivity of completely ionised KBr is 64·7 + 67·6 and of silver nitrate 54 + 61·8. These numbers agree well with the values directly determined.

In the case of weak electrolytes, i.e. those which are only slightly ionised at moderate dilution, it is not possible to determine the equivalent conductivities at "infinite" dilution, since the solutions would be too weak for accurate measurement. But we can calculate the value if we know the conductivities of the two ions. In calculating the degree of ionisation of a weak acid, for example, by the method given above, we require to know its equivalent conductivity at infinite dilution, and we can calculate this if we know the ionic conductivities of its anion and of hydrogen. Now it happens that the sodium salts even of the weakest acids are strongly ionised at moderate dilution. We can therefore measure the equivalent conductivity of the sodium salt at a dilution at which it is completely ionised and, subtracting the known value for sodium, we obtain that for the anion; adding to the latter the known value for hydrogen we get the required equivalent conductivity of the completely ionised acid.

98 a. The equivalent conductivities calculated in this way may also be employed in certain cases for the determination of the concentration of a solution. The solubilities of very sparingly soluble salts have been obtained in this way. The specific conductivity of the saturated solution is determined and, as the solution

is so dilute, it is assumed that the salt is completely ionised. If then we know U and V for the ions of the salt we can calculate the solubility, since $U + V$ is equal to the specific conductivity multiplied by the volume of the solution which contains one equivalent weight.

99. The *absolute* speed or mobility of the ions is extremely slow owing to the great frictional resistance which they experience in travelling through the liquid. Since each univalent ion carries the same charge, the force tending to drive it through the liquid, under a given fall of potential, is the same for each; but the frictional resistance is different for different ions and hence their speeds differ. The absolute *mobility of an ion* is defined as the speed, in centimetres per second, with which the ion moves under a fall of potential of one volt per centimetre. The values for the ions mentioned in the above list may be obtained by dividing the ionic conductivities by the charge carried, that is by 96,540; e.g. for hydrogen at 18° it is $\frac{318}{96540}$, or about 0·003 cm. per second. The absolute speeds may also be directly determined by taking advantage of the fact, which has been proved independently, that the ions travel with about the same speed in solid jellies as they do in water. If, for example, an acid is electrolysed in two vessels which are connected by a tube filled with agar-agar jelly and containing some indicator, such as slightly alkaline phenolphthalein, the rate at which the hydrogen ions travel is made apparent by the decolorisation of the indicator.

The ionic mobilities become greater as the temperature increases; also, the differences between their values tend to diminish with increase of temperature. This last fact has been explained by supposing that the ions are combined with a large number of molecules of water, the different frictional resistances experienced by various ions being due to the different number of water molecules combined. As the temperature increases these hydrates tend to become dissociated and the degrees of hydration become more equal.

CHAPTER IX

CONDUCTION OF ELECTRICITY IN GASES AND RADIOACTIVITY

100. Researches on the conduction and discharge of electricity in gases have, in recent years, led to many remarkable results which, although purely physical in character, have proved to be of fundamental importance in the development of theoretical chemistry. Incidentally, these results have also led to the discovery of radioactive substances and the two fields of investigation—electric conduction in gases and radioactivity—are found to be intimately connected. In what follows an attempt will be made to give a brief elementary account of some of the results of these investigations which are of particular importance in Physical Chemistry.

Conduction in gases. Gases under ordinary conditions of temperature and pressure are practically non-conductors of electricity. If a gas, under these conditions, is placed in a glass tube in which two metallic electrodes are sealed and the electrodes are connected with the terminals of an induction coil, nothing apparently happens unless the difference of potential is very great. If this amounts to some thousands of volts, electricity may pass as a "brush discharge" or as a spark; the difference of potential necessary to produce these effects depending on the nature of the gas, the pressure and the shape of the electrodes. As the pressure is reduced the discharge takes place much more readily.

As a rule however it can be shown by means of very delicate instruments that in air at ordinary pressures a certain amount of conduction does take place, even though no discharge passes, i.e. there is a slight "leak." By various means this conductivity can be increased very considerably; for example, by the influence of ultra-violet light, radium, Röntgen rays, etc. (see below). It is now believed that this conductivity is due to the presence of gaseous ions, which however are in many respects very different from the ions of an electrolyte in solution. The gas ions may be removed by filtration through cotton wool or by washing with water and can be blown about by currents of air; they behave in fact as if they were present as suspended material particles or dust. A gas which has been "ionised" by one of the agencies mentioned, if left to itself, gradually loses its conducting properties, i.e. the ions gradually disappear; this may be due to the recombination of the ions or to their charges being given up to solid bodies with which they come in contact.

101. *Cathode rays.* When an electric discharge is passed through a tube which has been partially exhausted, a bright glow is seen to cover the surface of the cathode (i.e. the electrode by which the current leaves). Beyond this is a dark space (called Crookes' dark space) and this is followed by a luminous portion and then another dark space (called Faraday's dark space); the remainder of the tube up to the anode is filled with a striated column of light (called the positive column). With a longer tube, the positive column is longer, the two dark spaces being in much the same position as before. If now the pressure of the gas is further diminished, the Crookes' dark space is seen to extend and, at a sufficiently low pressure, it fills the whole tube. On the walls of the tube opposite the cathode and on the anode, luminous phosphorescent effects are produced and, if a screen is interposed, a sharp shadow is cast. This shows that the luminous effects

must be produced by something in the nature of rays proceeding in straight lines from the cathode. The direction is independent of the position of the anode, which may be placed on one side so that the effect is all seen on the wall opposite the cathode. That these rays possess energy is evident from the fact that they may be made to do mechanical work; a small windmill, for example, may be turned if placed in their path. Also, they produce heating effects in the objects on which they strike. All evidence goes to show that these effects are produced by a stream of small particles which carry a negative charge. It is referred to as the *cathode stream* or the *cathode rays*. The rays may be deflected by a magnet and the direction in which they are deflected is that in which negatively electrified particles would move. If the deflected rays are caused to impinge upon an insulated metallic body, the latter becomes negatively electrified.

By measuring the deviations which these rays experience in electric and in magnetic fields, it is possible to calculate the velocity with which the particles move, and also the ratio of the charge (e) which they carry to their mass (m). The charge on a single particle has been estimated by experiments on the behaviour of these particles towards supersaturated vapour. When normally saturated aqueous vapour is suddenly expanded it becomes cooled and the space is now supersaturated. It will remain in this state for a considerable time if the space is free from dust or other particles; if however these are present they act as nuclei for the condensation of vapour and a mist is formed. The charged particles in an ionised gas behave in a similar manner and by estimating the size of the particles, the total quantity of water precipitated and the total quantity of electricity, it is possible to calculate the charge on a single particle.

The results of these experiments, performed in various ways, show that the mean velocity of ordinary cathode rays is about $\frac{1}{10}$ that of light, i.e. about 3×10^9 centimetres per second. The charge on a single particle is

about 10^{-19} coulombs and, from the values obtained for the ratio $\dfrac{e}{m}$, it can be calculated that the mass of the particle is about $\frac{1}{1000}$ that of the hydrogen atom.

The results obtained are the same no matter what is the nature of the metals, gases, etc. used in the instruments for producing the cathode rays.

102. *Electrons.* The charge on a single particle is the same as that carried by a univalent ion in solution. This we saw (Section 91) is quite invariable and is the same for all univalent ions; for n valent ions it is n times as great. The simplest way of explaining this is to suppose that electricity cannot be taken up continuously, but only in "parcels" or unit quantities (quanta). Just as we regard matter as existing in unit quantities or atoms, so we may conceive "atoms of electricity." These units or atoms of electricity are called *electrons* or *corpuscles.* [The names are now used for the *negative* units only; positive units are called by other names.]

It would, at first sight, appear meaningless to speak of the *mass* of a unit of electricity. But there is strong evidence to show that mass may be electrical in its nature. In order to move a body with a given velocity, a certain definite force is necessary; if now we charge the body with electricity the force required to move it with the same velocity as before is greater. If M is the mass and V the velocity, the kinetic energy of the uncharged body is $\dfrac{MV^2}{2}$; when it is charged and moves with the same velocity its kinetic energy is $\dfrac{(M+m)\,V^2}{2}$, i.e. it appears to have a mass $M + m$. This is because the charged body in moving creates magnetic force which opposes its motion and more energy is therefore required to move it with a given velocity than if it were uncharged. With large bodies moving slowly, this increase in the apparent mass is altogether insignificant; but as the size becomes

smaller and the velocity greater the increase becomes noticeable. In the case of exceedingly minute particles moving with a high velocity, approaching that of light, the "real" mass M becomes insignificant as compared with the "apparent" mass m. Now it appears probable that the mass of the corpuscles or electrons may be *all* of this electrical nature, i.e. that the whole of the observed mass is really an effect due to the electromagnetic "inertia" of the electric charge. It can, in fact, be shown that the mass of an electron does vary with its velocity. Although the average velocity of the cathode ray particles is about $\frac{1}{10}$ that of light, it is possible to separate out the more slowly moving particles (e.g. by passage through a thin plate of aluminium) and the particles remaining have a higher average velocity. Moreover negative corpuscles may be obtained from radium (see below) which appear to be identical in every way with those of cathode rays, except that they move much more rapidly. Now it has been shown by Kaufmann that the value of the ratio $\frac{e}{m}$ for these rapidly moving particles is less than for ordinary cathode rays and, assuming the charge e to be constant, m must be greater.

According to the more recent development of the theory, these electrons form the basis of all *matter*, and the chemical atom of matter may be regarded as a system of rapidly moving negative corpuscles whose mutual repulsion is balanced by an equivalent quantity of positive electricity.

103. *Röntgen rays or X rays.* The cathode rays, when they strike the wall of the glass vessel opposite the cathode, produce a green phosphorescence; if allowed to impinge on minerals many beautiful colour effects may be obtained. When the rays are stopped in this way it is found that a new kind of radiation is sent out in all directions from the spot. These new rays, discovered by Röntgen in 1895, can pass through many substances,

such as paper, thin sheets of aluminium, cloth, flesh, etc. They affect a photographic plate and excite phosphorescence in certain substances, such as barium platinocyanide or zinc silicate (willemite), and they "ionise" gases (see above). They undergo no deviation in a magnetic field or in an electric field; hence they cannot be electrically charged. Under certain conditions they may exhibit the phenomena of reflexion, interference and polarisation. The nature of these rays has been the subject of much discussion. They were formerly regarded as "pulses" in the ether, the pulse being generated by the sudden stoppage of the moving electron when it strikes an object. Another view was that they are neutral "doublets," consisting of a negative and a positive charge. Recent work has now demonstrated that they are light waves of extremely small wave length. All substances absorb these rays to some extent; the amount of absorption depending mainly on the density of the substance. On passing these rays through objects made up of parts having different densities, the rays will therefore be differently absorbed and the form of the denser parts can be photographed, or can be observed on a fluorescent screen, e.g. of barium platinocyanide. In this way we can photograph or observe, for example, the bones of the hand, coins in a leather purse or crystals in a heterogeneous alloy. It has recently been shown that the opacity of the elements for Röntgen rays is a function of the atomic weight, increasing as the atomic weight increases. The property appears to be additive, the specific opacity of a compound being equal to the sum of those of its constituents.

104. *Positive rays.* A tube for the production of cathode rays may be constructed in such a way that the cathode consists of a metal plate, drilled with fine holes, which fits right across the tube. When this tube is highly exhausted and a discharge is passed through it, slightly divergent bundles of luminous discharge are

seen to stream through the holes into the space behind the cathode.   These are called canal rays (*Kanalstrahlen*); they were first observed by Goldstein in 1886.   The colour of the rays depends on the nature of the gas which remains in the tube; air gives a yellowish colour, hydrogen a rose colour and neon a brilliant red; the colours are different from those which cathode rays produce.

The rays may be deflected by the influence of a very powerful magnetic or electric field, and the direction of this deflection is *opposite* to that produced in cathode rays, showing that the rays carry a positive charge. Where these rays strike the wall of the tube they produce phosphorescent effects, but the colour produced is different from that given by cathode rays.   The effects are best seen by allowing the rays to impinge on a screen of willemite; they also act upon a photographic plate. These rays appear to consist of streams of particles; it is supposed that, under the strong electric tension to which the gas has been subjected, the neutral molecules of the rarefied gas lose one or more negative particles, becoming thereby positively charged.

From the deviation which these rays experience in electric and in magnetic fields, it is possible to calculate the velocity of the particles and also the ratio of charge to mass $\left(\dfrac{e}{m}\right)$.   If the rays are subjected at the same time to an electric field and a magnetic field parallel to one another*, a ray issuing through a hole in the cathode plate will be deflected and its position may be recorded on a photographic plate.   If the particles all had the same velocity and the same value for $\dfrac{e}{m}$, the image recorded on the plate would be a single spot.   If, however,

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* The magnetic and electric deflections are then at right angles to one another; for a given value of $\dfrac{e}{m}$ they are inversely proportional, respectively, to the velocity and the square of the velocity of the particle.

the velocities are not all alike the image will appear as a line or band; if the value of $\frac{e}{m}$ is also different for different particles, the different parts become sorted out and the image on the plate will consist of a series of curves (parabolas) one above the other, each representing a given value of $\frac{e}{m}$. In many cases it can be proved that each particle carries a single charge and from the position of the curve on the plate one can then calculate at once the value of m. Carbon dioxide, helium and some other gases when examined in this way give the normal values, i.e. m is the same as the molecular weight calculated from the density. Nitrogen and oxygen give values corresponding to molecules N_2 and O_2 and also to single atoms. In hydrogen values are found corresponding to H_1, H_2 and H_3.

In some other cases it is necessary to assume that the particles carry more than one charge; mercury appears to carry eight charges, krypton four or five, argon three and neon two.

The study of these positive rays evidently affords a method of chemical analysis in that it tells us the molecular weight of the particles. The delicacy of this method is far greater than that of the spectroscope and it may be used even in mixtures of gases. In this way it was found possible to detect the presence of helium in 1 c.c. of atmospheric air; the quantity of helium present here is about three-millionths of a c.c.

For further details see Thomson, Bakerian Lecture, *Proc. Roy. Soc.*, 1913. Also *Rays of Positive Electricity* (Longmans).

105. Radioactive substances. The term *radioactivity* is now generally used in reference to the property which certain substances possess of spontaneously giving off radiations which are capable of affecting photographic plates and of "ionising" gases (i.e. of making gases

conductors of electricity). The discovery of such sub-
stances originated in the following way. Shortly after the
discovery of Röntgen rays, experiments were made with a
view of ascertaining whether these rays could be obtained
from substances which have fluorescent or phosphorescent
properties, since the Röntgen rays produce these pro-
perties on suitable screens. Becquerel in 1896, while
examining uranium compounds with this object, found
that potassium uranyl sulphate, after exposure to sunshine,
emitted rays which could affect a photographic plate,
even if the plate was covered with black paper. After-
wards he found that the preliminary exposure to sunshine
was unnecessary and that all compounds of uranium,
and the metal itself, gave off these rays, even if kept for
a long time in the dark; their production, in fact, has
nothing to do with phosphorescence. These rays, which
not only affect photographic plates but also ionise gases,
were called "uranium rays" or "Becquerel rays." They
were found to be of two kinds: one portion of the radiation
being easily absorbed by thin sheets of metal and the
other portion being more penetrating. Both are entirely
different from Röntgen rays since they are deflected in
a magnetic field. As a result of the discovery of uranium
rays, many investigations were undertaken with the
object of ascertaining whether any other substances
exhibited similar properties and these investigations led
to the discovery of radium and other radioactive
elements.

Thorium compounds were shown by Mme Curie to
behave like uranium compounds. But in this case the
remarkable observation was made that if the active
substance is dissolved in an acid and the thorium pre-
cipitated as hydroxide by ammonia, the filtrate contains
nearly all the radioactive constituent and the precipitate
is nearly inactive. The filtrate also yields an emanation
(see below), whilst the precipitate does not. But the
activity and emanating power of the filtrate soon begin
to fade and after about a month have completely

disappeared; whilst the precipitate at the same time *gains* activity and emanating power. The precipitate gains these properties at the same rate as the solution loses them, and after about a month the precipitate has recovered its original activity. If the precipitate is now dissolved again and is re-precipitated by ammonia, the same thing happens as before, nearly all the active constituent being contained in the filtrate and the fresh precipitate being nearly inactive. If the active filtrate is evaporated to dryness and the residue ignited, a small amount of substance remains which contains all the activity which the precipitate has lost; this substance is called thorium X.

These results are most easily accounted for in terms of the *disintegration theory* proposed by Rutherford and Soddy. It is supposed that the atoms of all radioactive elements are unstable and that, in a given time, a certain definite proportion of the atom breaks down explosively, the decomposition being accompanied by the expulsion of either negatively or positively charged particles, or both. The residue which is left is now the atom of a new substance which is quite distinct, chemically and physically, from the original substance and is, as a rule, itself unstable and undergoes further disintegration.

106. Mme Curie, whilst examining uranium and thorium minerals, made the important observation that the radioactivity of the mineral was, in most cases, much greater than that of the pure uranium or thorium compounds which could be obtained from the minerals, and it appeared therefore that the minerals must contain some more active constituents. By careful fractional separation these more active constituents were isolated. In pitchblende (a uranium mineral consisting principally of the green oxide U_3O_8) the small quantity of barium present was found to be associated with one highly active constituent (radium), the bismuth with another (polonium) and the thorium with another (actinium).

Radium, polonium and actinium are now considered to be degradation products of uranium. Boltwood has shown that in numerous uranium minerals the ratio of uranium to radium is constant; this supports the view that the radioactive element is being produced as well as being destroyed, and attempts are now being made to "grow" radium from pure uranium compounds.

Altogether about thirty distinct radioactive elements are said to be known. Of these, only radium and its emanation (niton) have been examined as elements by the ordinary chemical methods; the proof of the existence of the others is more or less indirect*. The methods employed for characterising these elements are of two kinds: the first depends on the examination of the kind of radiations and emanations emitted, and the second is based on observations of the rate at which the elements "decay."

107. α, β and γ rays. The radiations emitted by radioactive substances may be of at least three kinds. The α rays are the less penetrating, being unable to pass through a piece of paper or a few centimetres of air. They are considered to consist of atoms of helium carrying two positive unit electrical charges. Their velocity is about $\frac{1}{10}$ that of light. The β rays are much more penetrating, being able to get through thin plates of metal. They appear to be identical in every respect with cathode rays, except that their average velocity is much greater, nearly approaching that of light; they carry a negative charge.

The γ rays appear to be identical with very penetrating Röntgen rays. Like these, they were at first regarded as "pulses" in the ether or as neutral "doublets," but now they are believed to be light rays of exceedingly short wave length. They can pass through a considerable

* For a full account of these, and the discussion of their position in the Periodic table, see *The Chemistry of the Radio-Elements*, by F. Soddy. (Longmans.)

thickness of metal.   These three types of radiation may
be distinguished therefore by their differences in pene-
trating power, and also by their behaviour in a magnetic
field.   The positively charged α rays are deviated in one
direction, the negatively charged β rays in the opposite
direction and the γ rays are not deviated at all.

Emanations.   In addition to the emission of these
three types of radiation, radium, thorium and actinium
give off radioactive gases or "emanations."   These can
be expelled from the radioactive substance by heating to
a high temperature or, better, by dissolving the substance
and blowing a current of air through the solution.   The
air carries off the emanation and, in case of radium, by
passing the mixture through a vessel cooled by liquid
air the emanation may be condensed to a liquid or solid.
The radioactivity of these emanations is transient; that
from radium lasts a few days, whereas that from thorium
disappears after a few minutes, and from actinium after
a few seconds.   The emanation from radium is called
"niton"; its molecular weight has been estimated by
the direct determination of its density and also by the
method of diffusion (see Section 14).   It would appear
that the first stage in the degradation of the radium atom
(atomic weight 226·4) consists in its resolution into an atom
of emanation, with atomic weight 222·4 and an α particle,
i.e. a charged atom of helium (atomic weight 4).   [The
atomic weight of niton is considered to be the same as its
molecular weight because the general behaviour of these
emanations resembles that of the non-valent elements
whose molecules are monatomic.]

108.   *Rate of decay.*   All radioactive elements are,
according to theory, in a state of continual decomposition
or decay, and the specific rate at which this decomposition
takes place affords a most characteristic means of identi-
fying the element.   It is found that this rate of decay is
a reaction of the first order (compare Section 60 *a*), that is
to say, the rate of change at any instant is proportional

to the quantity of substance reacting. Thus if a is the quantity originally present and b is the quantity left after the time t has elapsed,

$$K = \frac{1}{t} \log_e \frac{a}{b}.$$

The velocity constant K has a definite value for each radioactive substance, and by its experimental determination we can use it for characterising the substance, just as we use the atomic weight or other constant in characterising elements in the usual way. It is the custom however to express the result in a somewhat different form, namely to determine the time which it would take for the substance to be half decomposed; that is, to determine the value of t when $\frac{a}{b} = 2$. The equation above may then be written

$$K = \frac{1}{t} \log_e 2.$$

The value of t is then known as the period of half decay and is used, instead of K, to characterise the substance.

The value of t for radium is about 1300 years and for radium emanation 3·8 days. For thorium X it is 3·7 days and for thorium emanation 76 seconds.

CHAPTER X

SOME APPLICATIONS OF PHYSICAL CHEMISTRY

109. The brief sketch which has been given in the
preceding pages may perhaps be brought to a conclusion
most suitably by some reference to the many and
important applications of Physical Chemistry. In the
rapid progress which has been made in many other
sciences during recent years, Physical Chemistry has
played an important part; one may mention for example
the numerous applications of the theories of solution and
of ionisation to Physiology, Botany and Medicine and of
the phase rule, and of radioactivity, to Geology.

In Technical Chemistry great advances have been made
through the intelligent use of the general laws and prin-
ciples of Physical Chemistry; new industries have been
created and many of the older processes have been
entirely revolutionised.

It is proposed here to give a few examples which may
indicate the way in which the application of these prin-
ciples can be of service in the correct interpretation,
classification and scientific working of well-known manu-
facturing processes.

Lime burning. This operation, the object of which is
to obtain quicklime from chalk, is probably one of the
oldest chemical processes, since the use of lime in mortar
can be traced back some thousands of years: yet the
nature of the process was never clearly understood until
the time of Deville's researches on dissociation. The

general character of the change, $CaCO_3 \rightleftarrows CaO + CO_2$, has already been discussed in Sections 26 and 33. In terms of the *phase rule* we have two components and three phases so that, if all of these phases are present, the system has one degree of freedom; for a given temperature therefore the carbon dioxide will have a definite maximum pressure. We arrive at the same conclusion by application of the law of *mass action*; since the lime and chalk are solids we regard their concentrations as being constant, so that the concentration (and therefore the pressure) of the carbon dioxide must also be constant (Section 63). Since heat is evolved when calcium oxide and carbon dioxide combine, we conclude, from the *principle of le Chatelier*, that the dissociation is greater at a higher temperature. By application of the formula given on page 127 we can calculate the heat of formation of chalk, if we know the dissociation pressures at two different temperatures.

From these general principles it is easy to see that in order to obtain lime from chalk a sufficiently high temperature must be employed to give an appreciable dissociation pressure. Now this pressure at 800° C. is about equal to the atmospheric pressure, so that if we wish the gas to diffuse quickly away, we cannot use a temperature much below this. In practice however a lower temperature may be used and the carbon dioxide swept away by a current of inert gas (e.g. air).

Brin's oxygen process, in which barium oxide is used in obtaining oxygen from the air, involves a reversible reaction entirely analogous to that which occurs in lime burning and the explanations are the same. Here however our object is to obtain the *gas* which is evolved, so that the actual details of working are different. The barium oxide is heated to about 500°–700° in air at a pressure of about two atmospheres; it is thus converted into barium peroxide; the residual nitrogen is removed, and the pressure is reduced to about $\frac{1}{20}$ atmosphere, the temperature being kept about the same. The resulting

oxygen is pumped out and the residual barium oxide used again. The explanation is that in the reversible change $2BaO_2 \rightleftarrows 2BaO + O_2$, the oxygen has a definite maximum pressure at a given temperature. This pressure at 525° is only 20 mm.; at 650° it is 65 mm.; at 720°, 210 mm.; at 750°, 340 mm. and at 790° it is 670 mm. Now the partial pressure of oxygen in the atmosphere at normal pressure is about 157 mm., so that at 650° the dioxide would not dissociate at all in air. We see then that a very high temperature would be necessary in order to dissociate the peroxide at a rapid rate at atmospheric pressure. But by keeping the temperature at about 700° and suitably increasing or diminishing the oxygen pressure, we can bring about the formation or dissociation of the peroxide at will.

This method of obtaining oxygen from the air has been largely superseded by the newer process of obtaining liquid air (Section 7) and submitting this to fractional distillation.

Contact process for sulphuric acid. The object of this process is to bring about the combination of sulphur dioxide and oxygen, the resultant sulphur trioxide being then combined with water to make sulphuric acid. The older attempts to employ this direct action as a commercial process were entirely unsuccessful owing to lack of the proper interpretation of general chemical principles. Very high temperatures were used in the first instance and even later, when the application of catalysis was appreciated, much labour was wasted in attempting to use only mixtures in the exact chemical ratio $2SO_2 : O_2$.

Studying the change from a theoretical standpoint we see that the best yield will be obtained by using a low temperature and excess of oxygen.

The reversible change $2SO_2 + O_2 \rightleftarrows 2SO_3$ is exothermic from left to right, i.e. heat is evolved when sulphur dioxide combines with oxygen; hence the yield of sulphur trioxide will be greater at a lower temperature. This has been confirmed experimentally also; thus the yield at

400° is about 98 per cent.; at 700°, 51 per cent. and at 900° only about 16 per cent.

Unfortunately, however, the *rate* of change is extremely small at 400°. We could of course increase the rate by raising the temperature, but we should then diminish the yield. The phenomenon of Catalysis comes to our assistance here; if we pass the mixed gases over a suitable catalyst, the change can be made to proceed at a conveniently rapid rate, even at this relatively low temperature. Note particularly that the presence of the catalyst does *not* increase the possible yield; it only alters the rate of change (Section 69). The substance employed here as catalyst is, usually, platinised asbestos, but certain other substances may also be used. Care has to be taken to purify the gases, otherwise the activity of the catalyst is impaired; traces of arsenic or mercury for example act as "poisons" in this way.

The "efficiency" of this process may be measured numerically as the ratio of sulphur trioxide produced to sulphur dioxide taken, the quantities being expressed in mols; i.e. as $\dfrac{SO_3}{SO_2}$. Now the law of mass action tells us that

$$[SO_2]^2 \times [O_2] \times K = [SO_3]^2,$$

where the numbers in square brackets represent the *concentrations* of the reacting substances and K is the reaction constant (see page 117).

Hence the efficiency of the reaction

$$\frac{[SO_3]}{[SO_2]} = \sqrt{[O_2]}K.$$

This shows at once that the efficiency will be somewhat greater if the relative oxygen concentration is increased or if the total volume is diminished, i.e. if the pressure is increased. The sulphur trioxide produced is continuously removed by absorption in strong (97—98 per cent.) sulphuric acid.

The direct synthetic production of ammonia. This process, which has recently been worked on a manufacturing scale, is comparable in many respects with the example last outlined. Ammonia is an exothermic compound, the change

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$
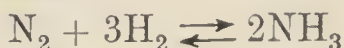
being attended with evolution of heat when it takes place from left to right. Evidently then, in order to obtain the best yield, we must carry out the operation at a low temperature. But here again the rate of change at low temperatures is exceedingly slow. Catalysts are therefore employed; uranium, osmium, manganese and iron appear to give the best results.

At 300° the change, even in the presence of catalysts, is too slow and a temperature of about 500°–700° has to be employed. The choice of this "optimum" temperature is, of course, of the greatest importance; one has to seek for the lowest possible temperature at which the reaction will proceed at a suitable rate. Since the combination is attended with diminution of volume, it is evident that increase of pressure will favour this change, i.e. it will shift the point of equilibrium from left to right. In practice a pressure of about two hundred atmospheres has been used. Here, as in the previous example, the resulting product is continuously removed as fast as it is formed, by absorption or by liquefaction.

Direct synthesis of oxides of nitrogen. Amongst the numerous methods which are employed for the purpose of utilising atmospheric nitrogen, one of the most important is that depending on the synthesis of nitric oxide. This product is further oxidised in presence of water to nitric acid or, in the presence of bases, to metallic nitrates.

The change

$$N_2 + O_2 \rightleftarrows 2NO$$
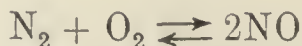
is attended with absorption of heat when it proceeds from left to right, i.e. nitric oxide is an *endothermic* compound. Consequently, the percentage of nitric oxide in the

equilibrium mixture will be greater at higher temperatures. Thus, it is found that at 1800° the percentage is about 0·37; at 2000°, 0·65; at 2580°, 2·05 and at 2675° it is about 2·23.

[These numbers have been determined experimentally. The percentage at any given temperature can also be calculated, if we have already determined the percentages at two different temperatures, by a modified form* of the equation given on page 127.]

By subjecting atmospheric air to very high temperatures, produced by means of an electric arc, we can therefore obtain a noticeable quantity of nitric oxide. But the rate of change, or "reaction velocity," is extremely rapid at such high temperatures, both for the forward and reverse change. Hence if we gradually cool down the mixture, recombination takes place and, by the time we have cooled it to atmospheric temperature, there will be practically no nitric oxide left. But if we very *suddenly* cool the mixture we can "slow up" the rate of change to such an extent that the system has not time to come to equilibrium and we can immediately fix and utilise our nitric oxide.

It is seen from the above relation that the combination of nitrogen and oxygen to nitric oxide takes place without change of volume. Hence we expect that alteration of pressure will make no difference in the final equilibrium state (Section 68); experiment shows that this is the case.

Increasing the concentration of either nitrogen *or* oxygen would increase the yield of nitric oxide obtainable from a given quantity of oxygen or of nitrogen, respectively. But that, of course, is not our object when we use atmospheric air. We do not mind how much air is wasted provided we obtain the desired quantity of our product; in practice, a rapid stream of air is used which immediately removes the product from the heated sphere.

* i.e. one has to take into consideration the variation of Q with T.

Producer gas is the name of the gaseous product obtained by the incomplete combustion of coke. It consists essentially of carbon monoxide and is used for heating purposes.

The reaction $C + O_2 = CO_2$ is, as has been previously stated, an exothermic change whereas the reversible change $CO_2 + C \rightleftharpoons 2CO$ is endothermic from left to right. If we pass a limited quantity of oxygen over excess of heated carbon, the final equilibrium system will consist of solid carbon in contact with a gaseous mixture of carbon monoxide and carbon dioxide, and the higher the temperature the greater will be the proportion of carbon monoxide in the mixture. Experiments indicate that at 1000° the equilibrium mixture is nearly all carbon monoxide and at 450° the gas is nearly all carbon dioxide. Evidently, in making producer gas one must employ a very high temperature.

Since the reverse action $2CO = CO_2 + C$ is nearly complete at 450°, it might be supposed that carbon monoxide should spontaneously break up at ordinary temperatures. The reason it does not do so is probably to be found in the slow rate of change. That this is the correct explanation seems probable from the fact that in the presence of a suitable catalyst (e.g. finely divided nickel) carbon monoxide does break down to carbon dioxide and carbon, even at such a low temperature as 250°.

In the preparation of *water gas,* steam is passed over heated carbon. The change may be either (1) $H_2O + C = CO + H_2$, or (2) $2H_2O + C = CO_2 + 2H_2$. The first is preferable for heating purposes, but the gas contains a large percentage of poisonous carbon monoxide. The second reaction is aimed at if we wish to use the change as a means of preparing hydrogen. Now by the application of general principles (the law of mass action and le Chatelier's principle) it is possible, from a few experimental data, not only to predict the direction of these changes but also to calculate the composition of the

mixtures which will be produced at a given temperature. It can be shown that at high temperatures the first reaction preponderates whilst at lower temperatures the result is mainly carbon dioxide and hydrogen.

Brief mention should also be made of the numerous applications of the laws and principles of Physical Chemistry to *Metallurgy*. New light has been thrown upon the changes which occur in many well-known metallurgical operations, with the result that important improvements have been effected in these processes. This is especially noticeable in the case of the iron and steel industries and here, as in many other cases, most important knowledge has also been gained by the scientific study of alloys (Section 31).

In the *separation of pure salts from mixtures* we are confronted with the difficult problems involved in the co-existence of different solid salts in contact with their aqueous solutions. As examples of this which occur in Chemical Industry we may mention (*a*) the preparation of pure potassium salts from the Stassfurt minerals, such as Carnallite; (*b*) the preparation of sodium bicarbonate from common salt by the Solvay process and (*c*) the manufacture of potassium nitrate from sodium nitrate. The successful solution of such problems has been very largely due to the application of theoretical principles, such as the phase rule and the theories of solution.

The systematic study of disperse systems (Section 29) has been the principal factor in the rapid development of *Colloid Chemistry* which has occurred in recent years. Very many large industries, such as those dealing with dyeing, tanning, explosives, rubber, celluloid and photographic emulsions, are intimately bound up with the chemistry of colloids and some of the most important advances which have been made in these industries are the direct outcome of purely scientific research in Physical Chemistry.

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